ASSESSMENT REPORT ON

AMMONIA

FOR DEVELOPING AMBIENT AIR QUALITY OBJECTIVES

- VOLUME I

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ASSESSMENT REPORT ON AMMONIA FOR DEVELOPING AMBIENT AIR QUALITY OBJECTIVES

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FOREWORD

Alberta Environment maintains Ambient Air Quality Objectives to support air quality management in Alberta. Alberta Environment currently has ambient objectives for thirty-one substances and five related parameters. These objectives are periodically updated and new objectives are developed as required. Fact Sheets on Ambient Air Quality Guidelines were updated in September 1997 and February 2000.

With the assistance of the Clean Air Strategic Alliance, a multi-stakeholder workshop was held in October 2000 to set Alberta's priorities for the next three years. Based on those recommendations, a three-year work plan ending March 31, 2004 was developed to review four existing guidelines, create three new guidelines for three families of substances, and adopt six new guidelines from other jurisdictions.

This document is one in a series of documents that presents the scientific assessment for these substances.

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NOTE: The *Environmental Protection and Enhancement Act*, Part 1, Section 14(1) refers to "ambient environmental quality objectives" and uses the term "guidelines" in Section 14(4) to refer to "procedures, practices and methods for monitoring, analysis and predictive assessment." For consistency with the Act, the historical term "ambient air quality guidelines" is being replaced by the term "ambient air quality objectives." This document was prepared as the change in usage was taking place. Consequently any occurrences of "air quality guideline" in an Alberta context should be read as "air quality objective."

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TABLE OF CONTENTS

FOREWORD i
ACKNOWLEDGEMENTS ii
LIST OF TABLES vi
LIST OF FIGURES vii
SUMMARY viii

1.0 INTRODUCTION 1

2.0 GENERAL SUBSTANCE INFORMATION 3
- 2.1 Physical, Chemical and Biological Properties 3
- 2.2 Atmospheric Chemistry and Fate 4
  - *2.2.1 Chemistry* *4*
  - *2.2.2 Fate and Transport* *4*

3.0 EMISSION SOURCES AND AMBIENT LEVELS 7
- 3.1 Natural Sources 7
- 3.2 Anthropogenic Sources 7
  - *3.2.1 Industrial* *7*
    - 3.2.1.1 NPRI Surveys 8
    - 3.2.1.2 National Inventories 13
  - *3.2.2 Agricultural* *13*
- 3.3 Other 18
- 3.4 Ambient Ammonia Levels in Alberta 18

4.0 EFFECTS ON HUMANS, ECOLOGICAL RECEPTORS AND MATERIALS 20
- 4.1 Humans and Animals 20
  - *4.1.1 Overview of Chemical Disposition* *20*
  - *4.1.2 Genotoxicity and Carcinogenicity* *21*
  - *4.1.3 Acute Effects* *21*
    - 4.1.3.1 Acute Adverse Health Effects in Experimental Animals 21
    - 4.1.3.1.1 Infection Susceptibility 24
    - 4.1.3.2 Acute Adverse Health Effects in Humans 24
    - 4.1.3.2.1 Accidental Human Exposures 24
    - 4.1.3.2.2 Controlled Human Exposures 25
  - *4.1.4 Chronic Effects* *25*
    - 4.1.4.1 Chronic Adverse Health Effects in Animals 26
    - 4.1.4.2 Chronic Adverse Health Effects in Humans 27
    - 4.1.4.2.1 Industrial Exposures 27
    - 4.1.4.2.2 Agricultural Exposures 28
    - 4.1.4.2.3 Ambient Air Exposures 29
  - *4.1.5 Summary Of Adverse Health Effects Of Ammonia Inhalation* *31*
- 4.2 Vegetation 31
  - *4.2.1 Effects of NH_3 and NH_4^+ (NH_y) on Vegetation* *32*
    - 4.2.1.1 Uptake of NH_y by Shoots and Roots 33
    - 4.2.1.2 Assimilation and Detoxification of NH_y. 33
    - 4.2.1.3 Metabolic Changes Due to NH_y Assimilation and Detoxification 34
    - 4.2.1.4 Changes in Leaf Gas Exchange Following Exposure to NHy. 34
    - 4.2.1.5 Effects of NHy on Epicuticular Waxes 34
    - 4.2.1.6 Factors Determining the Toxicity of NH_y 34

4.2.1.7 Direct Toxicity of NH_y and Visible Foliar Injury 35
4.2.2 Secondary Effects of NH_y Uptake and Assimilation on Vegetation *35*
4.2.2.1 Growth Responses 35
4.2.2.2 Resistance to Stress 35
4.2.3 Interactive Effects of NH_y with Other Air Pollutants on Vegetation *37*
4.2.4 Effects of N Deposition at the Ecosystem Level *37*
4.2.4.1 Soil Processes 37
4.2.4.2 Ecosystem Responses 38
4.2.5 Air Quality Indicators for Protecting Vegetation *39*
4.2.5.1 Critical Levels (NH_3) 40
4.2.5.2 Critical Loads (N) 41
4.2.6 Discussion *41*
4.3 Materials 43
4.3.1 Stone *44*
4.3.2 Brickwork, Mortar and Rendering *44*
4.3.3 Concrete *45*

5.0 RISK CHARACTERIZATION 46
5.1 Relevant Chemical Forms 46
5.2 Exposure Assessment 47
5.2.1 Humans *47*
5.2.2 Vegetation *47*
5.2.3 Materials *47*
5.3 Toxicity Assessment 47
5.3.1 Human Health *47*
5.3.1.1 Potential Health Effects of Exposure 47
5.3.1.2 Dose-Response Measures for Risk Assessment 48
5.3.2 Vegetation *48*
5.4 Characterization of Risk 49

6.0 AIR SAMPLING AND ANALYTICAL METHODS 51
6.1 Reference Methods 51
6.2 Alternative, Emerging Technologies 51

7.0 AMBIENT GUIDELINES 54
7.1 Canada 54
7.2 United States 56
7.3 European Union 56
7.4 Australia/ New Zealand 56

8.0 DISCUSSION 57
8.1 Acute Exposure Conditions 57
8.2 Chronic Exposure Conditions 59

9.0 REFERENCES 60

APPENDICES 80

LIST OF TABLES

Table 1 Identification of Ammonia ... 3

Table 2 Properties of Ammonia ... 5

Table 3 Natural Sources of Ammonia Emissions to Air in Canada (EC, 2000a; Geadah, 1985) ... 7

Table 4 Total Ammonia Emissions in Alberta According to NPRI, 1999 (in tonnes, ranked by total emissions) ... 9

Table 5 Ammonia Air Emissions in Alberta (NPRI, 1999) ... 11

Table 6 Ammonia Air Emissions, by Sector (NPRI, 1999) ... 12

Table 7 Ammonia Emissions to Air from Industrial Sources – Data for Canada and Alberta (EC, 2001a; EC, 2000; Geadah, 1985) ... 16

Table 8 Ammonia Emissions to Air from Agricultural Sources – Data for Canada and Alberta (EC, 2001a;EC, 2000; AAFC, 1998; Geadah, 1985) ... 17

Table 9 Range of Hourly Maximum Ammonia Concentrations at Selected Locations in Alberta ... 19

Table 10 Summary of Effects in Animals Following Acute Ammonia Exposure ... 23

Table 11 Summary of Effects in Humans Following Acute Ammonia Exposure ... 26

Table 12 Summary of Effects in Animals Following Chronic Ammonia Exposure ... 28

Table 13 Summary of Chronic Effects in Human Subjects Following Inhalation Exposure to Ammonia ... 32

Table 14 Critical Levels for Exposure of Vegetation to NH_3 ... 40

Table 15 Critical Loads for N ... 42

Table 16 Range of Estimated Critical Concentrations for Vegetation Exposure to NH_3 (summarized from Table 14) ... 49

Table 17 Method Advantages and Disadvantages ... 53

Table 18 Summary of Air Quality Guidelines for Ammonia (refer to Appendix C for agency reference) ... 55

LIST OF FIGURES

Figure 1 Total Ammonia Emissions by Province (includes emissions to air, water, land and underground) 14

Figure 2 Ammonia Air Emissions, by province 14

Figure 3 Trends in Ammonia Emissions from 1995 to 2002 15

Figure 4 Range of Exposure Concentration Guidelines for Ammonia Proposed by Various Agencies for Protection of Human and Ecological Receptors 50

SUMMARY

Ammonia is a naturally occurring, colourless, acrid-smelling gas. It is volatile and highly water-soluble. On a global scale, more than 99% of the ammonia present in the atmosphere is the result of natural processes. These natural processes consist mainly of biological degradation of organic matter, such as plants and animals, and chemical and microbial degradation of animal wastes, in particular urine. The major sources for atmospheric emissions of ammonia in Alberta would be agricultural activities (animal feedlot operations and other activities), followed by biomass burning (including forest fires) and to a lesser extent fossil fuel combustion (industrial sources) and accidental releases.

Two different types of potential health effects are considered important for ammonia: acute non-cancer effects that may result from short-term exposure and chronic non-cancer effects that may result from long-term exposure. Acute health effects reported in animals following short-term inhalation of ammonia include oral, nasal and eye irritation; respiratory tract irritation; decreased respiratory rate; increased respiratory depth; reduced body weight; and lethargy. These types of effects have been observed in controlled animal studies at concentrations ranging from 50 to 500 mg/m^3 (72 to 720 ppm) over exposure durations ranging from 6 hrs (continuously) to 40 hrs (intermittently over 5 days). Similar acute effects of ammonia inhalation are reported for humans (oral, nasal and eye irritation, and respiratory tract irritation) for comparable exposure concentrations and durations.

The health effects following chronic inhalation exposure of animals include nasal irritation; inflammatory response in lungs; reduced olfactory acuity; and lethargy. Animal studies have also demonstrated that ammonia exposure can reduce immune response and increase susceptibility to bacterial infection of the respiratory tract. These types of effects have been observed in controlled animal studies at concentrations ranging from 40 to 1,105 mg/m^3 (58 to 1,590 ppm) over exposure durations ranging from 24 to 90 days continuously. Chronic effects reported in humans include reduction in pulmonary function; cough; phlegm; wheeze, and dyspnea. These types of effects have been observed at an estimated exposure concentration equivalent to 50 mg/m^3 (72 ppm) over one year of occupational exposure.

Ammonia may affect vegetation directly by influencing the nitrogen cycling in ecosystems. Depending on the sensitivity of vegetation, exposure to ammonia may be harmful to plants. Adverse effects on vegetation occur when the rate of foliar uptake of ammonia is greater than the rate and capacity for *in vivo* detoxification by the plants. Most to least sensitive plant species are native vegetation, forests, and agricultural crops. The effect on materials from exposure to an individual air pollutant is difficult to separate from the effect of others. Many of the effects on materials have been ascribed more to the multi-pollutant situation that exists in urban environments than to the action of separate pollutants. Ammonia may be contributing to material damage in several ways, but its role is not yet clarified in the scientific literature.

Concentration-response levels in ambient air used for the protection of acute and chronic health effects in humans are on the same order as concentrations used for protecting vegetation. This

indicates that human health-based air quality criteria for ammonia may be adequate for protection of vegetation.

The current Alberta Environment 1-hour Ambient Air Quality Guideline for ammonia is 1,400 µg/m^3 (2,000 ppb) and based on odour perception. Manitoba Conservation also has a similar guideline and basis for development. The province of Ontario uses a maximum point of impingement guideline of 3,600 µg/m^3 (5,184 ppb) for a 30-minute averaging time. Acute ambient air guidelines used by jurisdictions in United States – for the most part – are based on non-cancer risk assessment of irritant effects to the respiratory system in humans.

The Alberta Environment 1-hour guideline appears to be adequate in protecting against reported acute effects of inhalation when compared to other short-term (≤ 24 hours) air quality guidelines developed using non-cancer risk assessment procedures. For example, Alberta Environment's 1-hour guideline is less than that adopted by state agencies in California (3,200 µg/m^3 or 4,600 ppb) and North Carolina (2,700 µg/m^3 or 3,900 ppb). State agencies in Ohio and Texas use a 1-hour guideline of 170 µg/m^3 (25 ppb) derived from the American Conference of Governmental Industrial Hygienists 8-hour Threshold Limit Value (17,000 µg/m^3 or 25 ppm).

Two state agencies, Louisiana and Vermont, use 8-hour guidelines ranging from 640 to 1,800 µg/m^3 (920 to 2,590 ppb) for specific purposes. Another four state agencies use 24-hour guidelines ranging from 100 to 1,742 µg/m^3 (144 to 2,480 ppb) for specific purposes. These include New Hampshire, Oklahoma, Washington, and Wisconsin. The approaches used for deriving 8-hour and 24-hour guidelines are based upon the American Conference of Governmental Industrial Hygienists 8-hour Threshold Limit Value or based upon non-cancer risk assessment of irritant effects to the respiratory system in humans.

A number of US agencies use air quality guidelines ranging from 17 to 208 µg/m^3 (25 to 300 ppb) applicable to chronic (≥1 year) exposure conditions for specific purposes. These include the US Agency for Toxic Substances and Disease Registry, US Environmental Protection Agency, and state agencies in California and Texas.

1.0 INTRODUCTION

Alberta Environment establishes Ambient Air Quality Guidelines under Section 14 of the *Environmental Protection and Enhancement Act* (EPEA). These guidelines are part of the Alberta air quality management system (AENV, 2000a).

The main objective of this assessment report is to provide a review of scientific and technical information to assist in evaluating the basis and background for an ambient air quality guideline for ammonia. The following aspects were examined as part of the review:

- physical and chemical properties,
- existing and potential natural and anthropogenic emissions sources in Alberta,
- effects on humans, animals, vegetation, and materials,
- characterization of risks to exposed receptors,
- monitoring techniques,
- ambient air guidelines in other Canadian jurisdictions, United States, European Union and Australia, and the basis for development and use

Important physical and chemical properties that govern the behaviour of ammonia in the environment include, but are not limited to, chemical structure, molecular weight, melting and boiling points, water solubility, density, vapour density, organic carbon partition coefficient, octanol water partition coefficient, vapor pressure, Henry's Law constant, bioconcentration factor and odor threshold. Values for these properties will be reviewed and presented in this report.

Existing and potential natural and anthropogenic sources of ammonia emissions in Alberta will also be presented. Natural emissions of ammonia are described in the literature. Anthropogenic emissions are provided in Environment Canada's National Pollutant Release Inventory (NPRI) and in several emissions inventories compiled by the Pollution Data Branch (PDB) of Environment Canada.

Scientific information about the effects of ammonia on humans and animals is reported in published literature and other sources. This information includes toxicological studies published in professional journals and reviews and information available through the US Agency for Toxic Substances and Disease Registry (ATSDR), and US Environmental Protection Agency's Integrated Risk Information System (IRIS), and the International Programme on Chemical Safety (IPCS). All of these sources provide valuable information for understanding health effects of ammonia exposure.

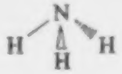
Reference air monitoring and other methods for detecting ammonia in air are also documented in published literature. In particular, several widely employed and accepted reference methods exist for ammonia. These methods have been developed, tested and reported by US National Institute for Occupational Safety and Health (NIOSH) and US Occupational Safety and Health Administration (OSHA).

Ambient air guidelines for ammonia are used by numerous jurisdictions in North America for different averaging-time periods. These guidelines are developed by using an occupational exposure level and dividing it by safety or adjustment factors, using non-cancer risk assessment procedures, or by basing it on a fraction of an odour threshold for humans. The basis for how these approaches are used by different jurisdictions to develop guidelines will be investigated in this report.

2.0 GENERAL SUBSTANCE INFORMATION

Table 1 provides a list of common synonyms and a list of important identification numbers for ammonia.

Table 1 Identification of Ammonia

Property	Value
Formula	NH_3
Structure	
CAS Registry number	7664-41-7
RTECS number	BO 0875000
UN Number	UN 1005
Common Synonyms	Anhydrous Ammonia Ammonium hydroxide Am-Fol Ammonia Gas Aqua Ammonia Nitro-Sil R717 Spirit of Hartshorn

According to the World Health Organization (IPCS, 1986), ammonia is one of the most widely used industrial chemicals. The most significant use of ammonia is as a fertilizer (ATSDR, 1990). Ammonia is an intermediate in the manufacturing of urea, ammonium nitrate, ammonium salts, nylon, acrylonitrile and isocyanate (Genium, 1999; Lewis, 1993). Ammonia is also used in the manufacturing of nitric acid, hydrazine, pesticides, detergents, explosives, fibers, plastics (Genium, 1999; IPCS, 1990; IPCS, 1986) and pharmaceuticals (ATSDR, 1990). Other industrial applications of ammonia include the chemical and refrigeration industry, the petrochemical industry, the rubber industry, water treatment, metal treating operations (Genium, 1999; ATSDR, 1990) and the food and beverage industry (ATSDR, 1990; IPCS, 1983).

2.1 Physical, Chemical and Biological Properties

The physical and chemical properties of ammonia are summarized in Table 2. Ammonia is a colourless, nonflammable, alkaline gas with a sharp, pungent and intensely irritating odour (Lewis, 2000; EC, 2000a; Genium, 1999; Lewis, 1993). Ammonia is very soluble in water, and once dissolved in water, it undergoes an acid-base reaction with water according to the following equation:

$$NH_4^+ \Leftrightarrow NH_3 + H_2O$$

The equilibrium constant for this reaction (Ka or pKa) is provided in Table 2. The species that exist in water are therefore NH_3 and NH_4^+, with NH_4^+ being the dominant form at neutral pHs. In the literature, NH_3 is referred to *un-ionized ammonia* and NH_4^+ is referred to as *ionized ammonia*. *Total ammonia* is the sum of both forms i.e. NH_3 and NH_4^+. When referring to ammonia in its gaseous state, the nomenclature used is ammonia gas, anhydrous ammonia or ammonia anhydre (EC, 2000a).

2.2 Atmospheric Chemistry and Fate

2.2.1 Chemistry

Gaseous NH_3 is a very important basic compound in the atmosphere. It reacts readily with acidic substances such as sulphuric acid (H_2SO_4), nitric acid (HNO_3), nitrous acid (HNO_2), hydrochloric acid (HCl) or sulphur dioxide (SO_2) to form ammonium salts that occur predominantly in the fine particle (size < 2.5 µm) fraction (EC, 2000b; Finlayson-Pitts and Pitts, 1999). The equilibrium relationships that describe the reactions of ammonia with HNO_3 and HCl are given below (EC, 2000b):

$$NH_{3\,(g)} \quad + \quad HNO_{3(g)} \quad \Leftrightarrow \quad NH_4NO_3$$

$$NH_{3\,(g)} \quad + \quad HCl_{(g)} \quad \Leftrightarrow \quad NH_4Cl$$

A small amount of gaseous NH_3 (approximately 1%) reacts with hydroxyl (OH) radicals to form NH_2 and H_2O, which is subsequently oxidized to NO by HNO_3 (EC, 2000b; Galbally and Roy, 1983). Relationships describing the reaction of NH_3 with these contaminants and with more than one contaminant are provided in EC (2000b).

The formation of fine particulate NH_4^+ salts is a very effective mechanism in removing gaseous NH_3 from the atmosphere. Estimates of the conversion rates of NH_3 to NH_4^+ vary between $10^{-3}\ s^{-1}$ (Vermetten et al., 1985) and $5x10^{-5}\ s^{-1}$ (Erisman et al., 1988). This conversion is most effective in the lowest (100 m) layer of the atmosphere above the surface (Lenhard and Gravenhorst, 1980) and is much faster during the daytime than at night (Erisman et al., 1988).

2.2.2 Fate and Transport

Since NH_3 is either readily converted to NH_4^+ or subjected to dry deposition, high concentrations are found only close to the surface and near to emission sources. With discrete or isolated NH_3 sources, concentrations decrease significantly within the lower 200 m of the atmosphere (Vermetten et al., 1985; Erisman et al., 1987) and can reach background levels at 1500 m in the winter and 3000 m in the summer (Georgii and Müller, 1974; Georgii and Lenhard, 1978; Lenhard and Gravenhorst, 1980; Levine et al., 1980; Alkezweeny et al., 1986). Horizontal concentration profiles show a clear decrease with increasing distance from the source (50% reduction at 600 m from the source (Erisman et al., 1987) and 70% decrease at 4 km (Asman et al., 1989)). Different estimates have been reported for the residence time of NH_3 ranging from 2.8 h during the daytime and 5 h at night (Erisman et al., 1988), 0.8 days (Möller and Schieferdecker, 1985), 1-4 days (Söderlund and Svensson, 1976) and 4 days (Dawson, 1984).

Table 2 Properties of Ammonia

Property	Value	Reference
Molecular weight	17.03	Lide, 2001
Physical state	Gas	Lide, 2001
Melting point	-77.7	Lide, 2001; IPCS, 1990; IPCS, 1986
Boiling point	-33.35	Lide, 2001; IPCS, 1990
	-33.42	IPCS, 1986
Specific gravity (liquid)	682.8 g/L @ -33.7°C, 100 kPa	EC, 2000a
Specific gravity (gas) (air =1)	0.6	Lewis, 2000
	0.696 g/L	Lide, 2001
	0.59	Genium, 1999
Vapour pressure	1013 kPa @ 25.7°C	Verschueren, 2001; Lewis, 2000
	1000 kPa @ 25°C	EC, 2000a
	1013 kPa @ 25°C	IPCS, 1986
	861 kPa @ 20°C	Lewis, 1993
Solubility in water	895 g/L @ 0°C, 1 atm	Verschueren, 2001; EC, 2000a; IPCS, 1986
	529 g/L @ 20°C, 1 atm	EC, 2000a; IPCS, 1986
	531 g/L @ 20°C, 1 atm	Verschueren, 2001
Solubility	Soluble in ether, alcohol	Lide, 2001; Lewis, 1993
pKa	0.09018 + 2729.2/T*	IPCS, 1986
	9.24 @ 25°C	EC, 2000a
Henry's Law constant	1477.8/T – 1.6937*	IPCS, 1986
	0.76	Genium, 1999
	7.3x10^{-6} atm.m^3.mol^{-1}@ 23.4°C, pH 7	ATSDR, 1990
	1.6x10^{-5} atm.m^3.mol^{-1} @ 25°C	
	5.01x10^{-6} atm.m^3.mol^{-1}@ 5°C	
Octanol water partition coefficient (log K_{ow})	-1.14	Genium, 1999
Flash point (closed cup)	Indefinite < 0°C	Genium, 1999
Explosive limits	16 to 25%	Lewis, 2000; Genium, 1999; ATSDR, 1990; IPCS, 1990
Autoignition temperature	650°C	Lewis, 2000; Lewis, 1993; ATSDR, 1990
	651°C	Genium, 1999
Odour threshold	46.8 ppm	Genium, 1999
	0.7 to 50 ppm	NRC, 1979
	5 ppm (average)	
	20 ppm (complaint level)	
	25 ppm, 48 ppm	ATSDR, 1990
	0.043 to 53 ppm	Ontario MOE, 2000
	17 ppm	
	10 mg/m^3	IPCS, 1986
Conversion factors for vapour (at 25 °C and 101.3 kPa)	1 mg/m^3 = 1.44 ppm 1 ppm = 0.707 mg/m^3	Verschueren, 2001; ATSDR, 1990

T = temperature

In the atmosphere, laws of gravity do not readily influence fine particle deposition on to surfaces. They are transferred on to surfaces by Brownian motion and thus ammonium sulfate [$(NH_4)_2SO_4$] and ammonium nitrate [NH_4NO_3] have low deposition velocities and prolonged atmospheric residence times. Assuming an atmospheric residence time of 6 days and a wind velocity of 5 m s^{-1}, the transport distance of $(NH_4)_2SO_4$ and NH_4NO_3 may be as large as 2,500 km (Irwin and Williams, 1988).

Vertical profiles of NH_4^+ concentrations are far less pronounced than NH_3. In contrast to NH_3 (high concentrations close to the surface), NH_4^+ concentrations were found to be higher than NH_3 at heights above 200 m (Georgii and Lenhard, 1978; Lenhard and Gravenhorst, 1980; Vermetten et al., 1985; Erisman et al., 1987, 1988). Horizontal profiles of NH_4^+ were also rather homogeneous (Allen et al., 1988; Janssen et al., 1989) with only relatively small increases near NH_3 sources (Vermetten et al., 1985). Estimates of the residence time of NH_4^+ were 4-7 days (Bonis et al., 1980), 7.7 days (Möller and Schieferdecker, 1985), 7-19 days (Söderlund and Svensson, 1976) and 15 ± 9 days (Böttger et al., 1978).

3.0 EMISSION SOURCES AND AMBIENT LEVELS

3.1 Natural Sources

On a global scale, more than 99% of the ammonia present in the atmosphere is the result of natural processes (IPCS, 1986; NRC, 1979). These natural processes consist mainly of biological degradation of organic matter, such as plants and animals, and chemical and microbial degradation of animal wastes, in particular urine. In the biological degradation of organic matter, ammonia is produced when proteins and nucleic acids are degraded to form amino acids, purines and pyrimidines (Geadah, 1985). Chemical or microbial degradation of animal urine leads to urea hydrolysis and then subsequently to ammonia volatilization (Geadah, 1985). Other natural sources of ammonia include vegetation, forest fires and human breath (Geadah, 1985)

The natural sources contributing to ammonia air emissions in Canada are presented in Table 3. In Table 3, biological litter refers to biological degradation of organic matter and wild and domestic animals refers to the chemical and microbial degradation of animal wastes.

Table 3 Natural Sources of Ammonia Emissions to Air in Canada (EC, 2000a; Geadah, 1985)

Source	Ammonia Emissions (tonnes)		
	1980	1990	1995
Biological Litter	454,171	458,386	458,386
Wild and Domestic Animals	35,407	43,993	43,993
Vegetation	NA	NA	NA
Forest Fires	15,911	2,989	15,023
Human Breath	134	7,032	7,554
TOTAL	505,623	512,400	524,956

NA – not available

3.2 Anthropogenic Sources

As stated previously, most of the ammonia occurring in the atmosphere is produced naturally however several anthropogenic sources exist. Anthropogenic sources include industrial sources, non-industrial fuel combustion sources, transportation, and incineration. Other miscellaneous anthropogenic sources include agriculture (i.e. animal husbandry), pesticide and fertilizer application, cigarette smoking and prescribed burning (EC, 2001a; Geadah, 1985).

3.2.1 Industrial

Industrial sources of ammonia are provided in the National Pollutant Release Inventory (NPRI) surveys. The NPRI program collects information from a wide variety of industrial and non-industrial sectors (EC, 1999c) but it does not include sources such as fuel combustion sources and mobile sources (i.e. automobiles and trucks) (EC, 1999c). Very few animal husbandry sources and few municipal sewage treatment plants are included in the NPRI survey (EC, 2000a). Environment Canada has conducted two national inventories for ammonia, one in 1980 (Geadah, 1985) and one in 1995 (EC, 2001a). These inventories provide ammonia emissions by province for most industrial sources including some not covered by the NPRI surveys.

3.2.1.1 NPRI Surveys

According to NPRI (1999), 333 facilities in Canada reported ammonia emissions in 1999. Of these 333 facilities, 54 are located in Alberta. These facilities are listed in Table 4 and are ranked according to total ammonia emissions. In general, most ammonia emissions are to air or underground. Agrium Inc. and Canadian Fertilizers are the two substantial emitters of ammonia to air. Syncrude Canada also emitted a significant amount of ammonia to air in 1999, however these 1999 emissions represented a 34.4% decrease on their 1998 emissions (EC, 1999a). Shell Canada, Petro Canada, Imperial Oil and Agrium also contributed substantially to underground emissions of ammonia. For Petro-Canada and Agrium, the 1999 emissions represented a substantial increase on the 1998 emissions (EC, 1999a). In the case of Petro-Canada, no explanation was provided by the facility. In the case of Agrium, the facility explained the increase in emissions as a result of accelerated remediation activities and not as a result of ongoing continuous operations at the facility (EC, 1999a).

As shown in Table 5, only 26 of the 54 facilities in Alberta report air emissions of ammonia. These emissions are principally stack or point source emissions (90.5% of the total air emissions), with some fugitive (5.5% of the total air emissions) and non-point source emissions (3.2% of the total air emissions). Stack or point source emissions include releases from stacks, vents, ducts, pipes, pollution-control equipment or other confined process streams. Fugitive emissions include emissions not released through confined process streams. These emissions include emissions due to leaks, evaporative losses, releases from building ventilation systems and other releases from land treatment, mine tailings, etc. Other non-point source emissions include emissions not included in the other categories identified in Table 5 (EC, 1999b)

Table 6 provides ammonia air emissions, reported by industrial sectors. In Table 6, "Other sectors" pertains to sectors reporting ammonia emissions in Canada but not reporting ammonia emissions in Alberta. These sectors include local government service industries, mining industries, industrial and heavy engineering construction industries, electrical and electronic parts industries, wood industries, transportation equipment industries, textile product industries, motor vehicle parts and accessories wholesale, beverage industries, rubber products industries, business service industries, plastic products industries and other products and industries (wholesale). Table 6 shows that the Chemical and Chemical Products sector is the most significant sector responsible for ammonia air emissions. This sector contributes 76.0% of the total Canadian air emissions and 81.3% of the total Alberta air emissions. Industries included in this sector are the agricultural chemicals industries, in particular the chemical fertilizers industries, and the industrial chemicals industries.

As shown in Figures 1 and 2, in 1999 Alberta released the largest quantities of ammonia in Canada. Environment Canada (2000) also reports the same for 1996. These large releases are due to the presence of a large number of fertilizer manufacturing facilities, pulp and paper mills and petroleum refineries (EC, 2000a).

Focusing on Alberta alone, ammonia is the pollutant released in the largest quantities in the province (NPRI, 1999; NPRI, 1998; NPRI, 1997). Figure 3 illustrates both Canadian and Albertan trends in ammonia emissions since 1995. In general, the total ammonia emissions (i.e. emissions to air, water, land and underground) in Canada and more specifically in Alberta have

Table 4 Total Ammonia Emissions in Alberta According to NPRI, 1999 (in tonnes, ranked by total emissions)

NPRI ID	Company	City	Ammonia Emissions (tonnes)				
			Air	Water	Land	Underground	Total
2134	Agrium Products Inc.	Redwater/Municipal District Of Sturgeon	2566 650	13.160	4.640	1441.630	4026.080
2960	Shell Canada Products Limited	Fort Saskatchewan	0	0.170	0	2978 000	2978.170
3821	Canadian Fertilizers Limited	Medicine Hat	2347 075	22 302	0	0	2369 377
3903	Petro-Canada	Edmonton	0	0 565	0	1993.733	1994.298
3269	Agrium Inc.	Calgary	1723.400	0	1 400	0	1724 800
4874	Agrium	Fort Saskatchewan	498.400	0	0	1123.000	1621 400
2274	Syncrude Canada Ltd	Fort McMurray	1061 690	0	0	0	1061 690
3707	Imperial Oil	Edmonton	0	0.462	0	861 285	861 747
2132	Sherritt International Corporation	Fort Saskatchewan	441.219	57.828	0.165	0	499.212
5309	City Of Calgary - Wastewater & Drainage	Calgary	0	352.000	0	0	352.000
5232	Lakeside Feeders Ltd	Brooks	0	0	338.000	0	338.000
4868	The Cobalt Refinery Company Inc	Fort Saskatchewan	203.522	14.945	0.018	0	218 485
5308	City Of Calgary - Wastewater & Drainage	Calgary	0	211 000	0	0	211 000
0947	Rogers Sugar Ltd	Taber	61 500	18.710	29 200	0	109 410
0223	Daishowa-Marubeni International	MD Of Northern Lights	94.741	0	0	0	94.741
2282	TransAlta Utilities Corporation	Wabamun	94.000	0	0	0	94.000
2630	Johns Manville Canada Inc.	Innisfail	73 413	0	0	0	73.413
2875	Weyerhaeuser Canada Ltd	Grande Prairie	43 905	28.180	0	0	72 085
0001	Alberta-Pacific Forest Industries Inc	Boyle	54 385	6 307	0	0	60 692
1033	Atco Electric	Forestburg	0	42.067	0	0	42 067
1251	Owens-Corning Canada Inc	Edmonton	28.908	0 051	0	0	28 959
2749	City Of Medicine Hat	Medicine Hat	0	21.590	1 160	0	22 750
4885	The Westaim Corporation	Fort Saskatchewan	21.964	0	0	0	21.964
1175	Agrium	County Of Lacombe	20.583	0	0	0	20.583
2857	Orica Canada Inc	Carseland	20 100	0	0	0	20 100
5235	Cargill Foods	High River	4 500	5 374	0.026	0	9.900
3758	Petro-Canada	Edson	6 935	0	0	0	6 935
2316	Union Carbide Canada Inc.	Red Deer	0	4.870	0	0	4 870
0878	Millar Western Forest Products Ltd.	Whitecourt	0 158	4.050	0	0	4 208
0280	Dow Chemical Canada Incorporated	Fort Saskatchewan	0	2.307	1 314	0	3.621
3959	Slave Lake Pulp	Slave Lake	0	3.220	0	0	3 220
0683	Chevron Canada Resources	Fox Creek	2 937	0	0	0	2 937
4884	Umex Inc.	Leduc	2.200	0	0	0	2 200
3910	Epcor Water Services	Edmonton	0	1.897	0	0	1.897

Table 4 Total Ammonia Emissions in Alberta According to NPRI, 1999 (in tonnes, ranked by total emissions) (continued)

NPRI ID	Company	City	Ammonia Emissions (tonnes)				
			Air	Water	Land	Underground	Total
3912	Epcor Water Services	Edmonton	0	1.481	0	0	1.481
2230	Suncor Energy Inc	Fort McMurray	0	1 420	0	0	1.420
2376	Western Co-Operative Fertilizers Limited	Calgary	1.183	0	0	0	1 183
1028	Alberta Newsprint Company	Whitecourt	0	0.518	0	0	0.518
4721	Enerchem International Inc	Nisku	0	0	0	0	0 450
0011	Borden Chemical Canada Ltd.	Edmonton	0	0	0	0	0 425
4567	Nalco/Exxon Energy Chemicals Canada Inc.	Nisku	0 168	0	0	0	0 168
0853	Marsulex Inc.	Fort Saskatchewan	0.100	0	0	0	0 100
5322	United Grain Growers	Camrose	0	0	0	0	0.100
5321	United Grain Growers Limited	Vermilion	0	0	0	0	0.100
5331	Untied Grain Growers Limited	Rycroft	0	0	0	0	0 100
0250	Degussa Canada Ltd	Gibbons	0	0.037	0	0	0 037
2183	Hci Stanchem Inc (As55)	Leduc	0	0	0	0	0 029
2128	Shell Canada Limited	Peace River	0 002	0 002	0.004	0	0 008
5715	Hci Stanchem Inc (Aw10)	Leduc	0	0	0	0	0 001
5307	City Of Calgary - Wastewater & Drainage	Calgary	0	0	0	0	0
4867	Burns Philp Food Limited	Calgary	0	0	0	0	0
1782	Methanex Corporation	Medicine Hat	0	0	0	0	0
3088	Rw Packaging Ltd	Edmonton	0	0	0	0	0
5284	Talisman Energy Inc	Edson	0	0	0	0	0
Total for the media (tonnes)			9373.6	814.5	375.9	8397 6	18962 9
Total for the media (as % of total emissions)			49 4	4.3	2 0	44.3	100

Table 5 Ammonia Air Emissions in Alberta (NPRI, 1999)

NPRI ID	Company	City	Ammonia Air Emissions (tonnes)					
			Stack /Point	Storage /Handling	Fugitive	Spills	Other Non-Point	Total
2134	Agrium Products Inc.	Redwater/Municipal District of Sturgeon	1971.550	0.100	235.000	60	300	2566 650
3821	Canadian Fertilizers Limited	Medicine Hat	2300 914	1.180	43 688	1.293	0	2347.075
3269	Agrium Inc.	Calgary	1702.400	2 800	18.200	0	0	1723 400
2274	Syncrude Canada Ltd	Fort McMurray	1061.690	0	0	0	0	1061.690
4874	Agrium	Fort Saskatchewan	434.700	0	63.200	0 500	0	498.400
2132	Sherritt International Corporation	Fort Saskatchewan	394 830	0	43 636	0	2 753	441 219
4868	The Cobalt Refinery Company Inc.85 85	Fort Saskatchewan	137 577	0	64 445	1 500	0	203.522
0223	Daishowa-Marubeni International	MD of Northern Lights	94 741	0	0	0	0	94 741
2282	TransAlta Utilities Corporation	Wabamun	94.000	0	0	0	0	94.000
2630	Johns Manville Canada Inc	Innisfail	55 911	0	17.502	0	0	73.413
0947	ROGERS SUGAR LTD	Taber	61.500	0	0	0	0	61.500
0001	Alberta-Pacific Forest Industries Inc.	Boyle	54 385	0	0	0	0	54.385
2875	Weyerhaeuser Canada Ltd	Grande Prairie	43 905	0	0	0	0	43 905
1251	Owens-Corning Canada Inc	Edmonton	26 374	0 384	2.150	0	0	28 908
4885	The Westaim Corporation	Fort Saskatchewan	21 835	0 129	0	0	0	21 964
1175	Agrium	County of Lacombe	3 983	0	16 600	0	0	20.583
2857	Orica Canada Inc	Carseland	19.900	0 100	0 100	0	0	20 100
3758	Petro-Canada	Edson	0	0	6 935	0	0	6 935
5235	Cargill Foods	High River	0	0	4.400	0 100	0	4 500
0683	Chevron Canada Resources	Fox Creek	0	0	2.937	0	0	2.937
4884	Umex Inc	Leduc	2.200	0	0	0	0	2.200
2376	Western Co-operative Fertilizers Limited	Calgary	0	0.597	0 586	0	0	1 183
4567	Nalco/Exxon Energy Chemicals Canada Inc	Nisku	0	0	0 168	0	0	0 168
0878	Millar Western Forest Products Ltd	Whitecourt	0	0.158	0	0	0	0 158
0853	Marsulex Inc	Fort Saskatchewan	0 100	0	0	0	0	0 100
2128	Shell Canada Limited	Peace River	0	0	0	0 002	0	0.002
Total for the source (tonnes)			8482 495	5 448	519 547	63 395	302 753	9373.638
Total for the sources (as % of total air emissions			90 5	0 1	5.5	0 7	3 2	100 0

Table 6 Ammonia Air Emissions, by Sector (NPRI, 1999)

SIC Code	Sector	Canadian Ammonia Emissions		Alberta Ammonia Emissions		% of Total Emissions for Alberta
		# of Facilities Reporting	Air Emissions (tonnes)	# of Facilities Reporting	Air Emissions (tonnes)	
37	Chemical and Chemical Products	94	13,160 430	22	7,618.878	57.9
7	Crude Petroleum and Natural Gas Industries	7	1071.573	6	1,071.564	100.0
29	Primary Metal Industries	11	649.218	1	203 522	31 3
27	Paper and Allied Products Industries	77	1,738.566	6	193 189	11 1
35	Non-metallic Mineral Products Industries	7	190.548	2	102 321	53 7
49	Other Utility Industries	32	146 067	8	94.000	64.4
10	Food Industries	18	139 457	4	66.000	47.3
39	Other Manufacturing Industries	4	24 464	2	24 164	98.8
36	Refined Petroleum and Coal Products Industries	17	63 008	3	0	0 0
NA	Other sectors	66	130.755	0	0	0 0
		333	17,314.086	54	9,373.638	54.14

increased since 1995 (NPRI, 1999, 1998, 1997, 1996, 1995). NPRI (1999) also predicts that the total ammonia emissions will remain relatively constant in the future. This prediction is based on estimates provided by the facilities as part of the reporting for NPRI. For the 1999 National Pollutant Release Inventory, facilities were required to provide estimates for total emissions for 2000, 2001 and 2002 total emissions but estimates for 2003 and 2004 were optional. Therefore, although estimates for 2003 and 2004 ammonia emissions are provided in the 1999 inventory, the data was not included here. Figure 3 also shows that air emissions of ammonia in Canada have remained relatively constant from 1995 to 1999. Alberta air emissions have followed this national trend.

In reference to the discussion above, it should be noted that not all facilities emitting ammonia are required to report to the NPRI. Only facilities meeting all three of the following criteria must report to the NPRI (NPRI, 1999):

- the facility has more than 10 full-time employees,
- the facility manufactured, processed or used 10 tonnes or more of an NPRI substance in the calendar year,
- the facility manufactured, processed or used an NPRI substance at a concentration greater than or equal to 1% by weight

Therefore, it may be possible that, in Alberta, ammonia is emitted by facilities that are not required to report to NPRI.

3.2.1.2 National Inventories

Table 7 summarizes the results of ammonia emissions tabulated for 1980 (Geadah, 1985) and 1995 (EC, 2001a) ammonia emissions inventories. Although each of these surveys provides a breakdown of emissions for all provinces, only the results for Alberta and Canada are presented here.

3.2.2 Agricultural

Agricultural emissions of ammonia for Canada and Alberta are tabulated in Table 8. Data for 1980 (Geadah, 1985), 1990 (EC, 2000a; AAFC, 1998) and 1995 (EC, 2001a; EC, 2000a) emissions are provided for Canada. Only 1980 (Geadah, 1985) and 1995 (EC, 2001a) emission data were available for Alberta. No data was available for ammonia emissions from crops in any of the reviewed studies.

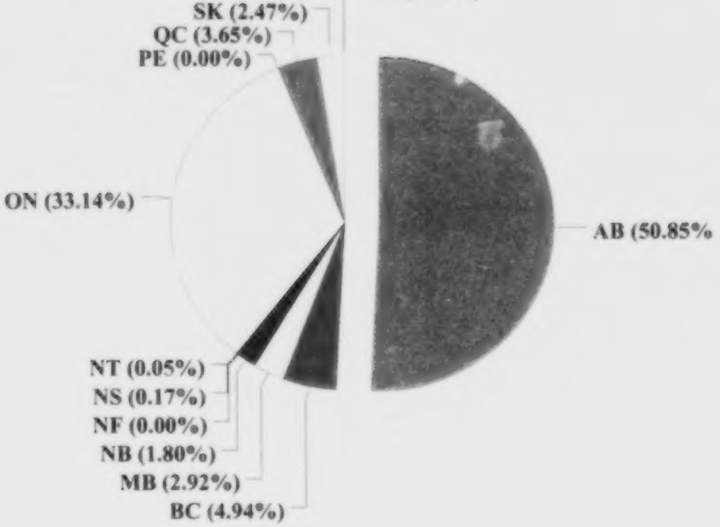


Figure 1 Total Ammonia Emissions by Province (includes emissions to air, water, land and underground) (NPRI, 1999)

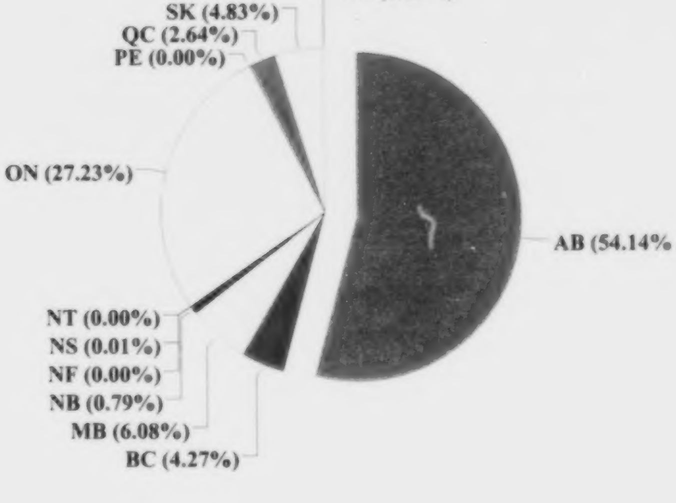


Figure 2 Ammonia Air Emissions, by province (NPRI, 1999)

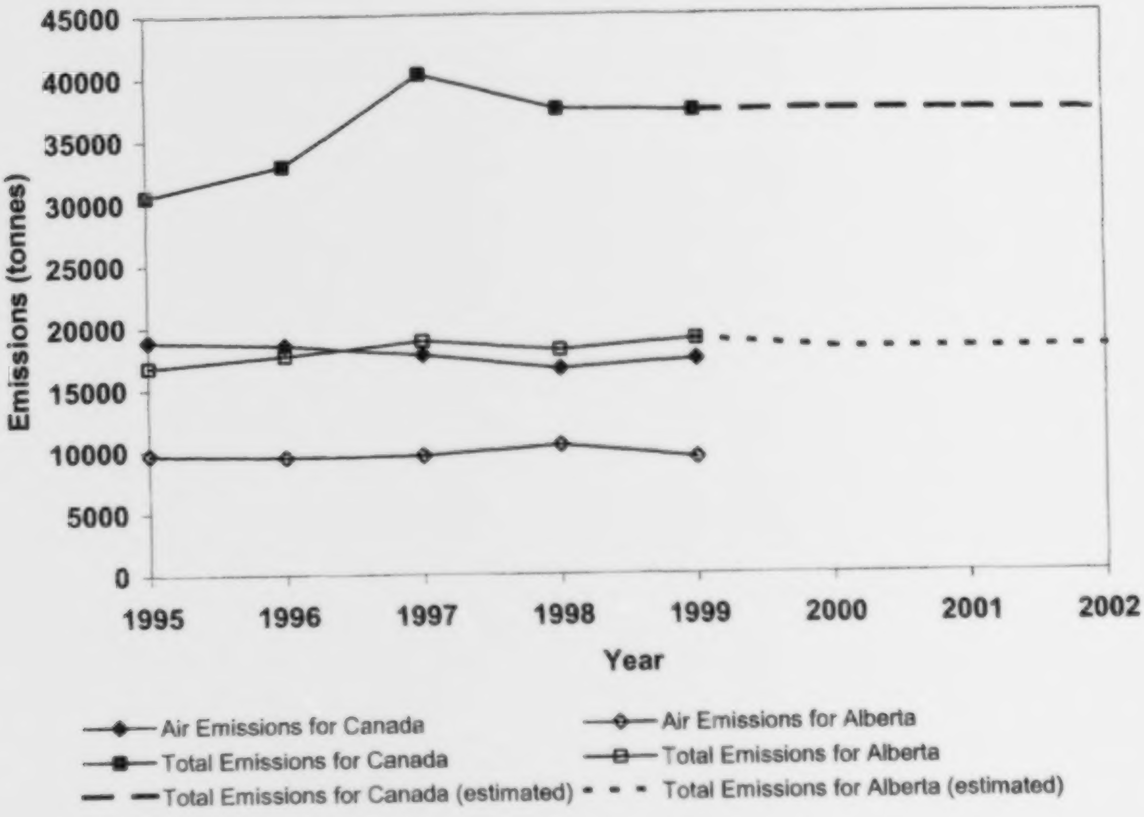


Figure 3 **Trends in Ammonia Emissions from 1995 to 2002 (NPRI, 1995,1996,1997,1998,1999)**

Agricultural sources of ammonia include animal husbandry, fertilizer application and crops (EC, 2000a; AAFC, 1998). Environment Canada (2001a) does not provide a detailed breakdown of the ammonia emissions for the animal sector or for the pesticide and fertilizer application sector. According to Environment Canada (2001a), the emissions included in the animals category includes ammonia emissions from six classes of livestock including cattle and calves, hogs and pigs, sheep and lambs, poultry, horses and ponies and other livestock. The other livestock category consists of mink, foxes, goats, rabbits and deer and elk. For each livestock class, NH_3 estimates were calculated at the grazing/outdoors, housing, manure storage and manure land-spreading stages using data on Canadian manure management techniques and farming practices, when available (EC, 2001b).

The data presented in Table 8 indicates that animal husbandry, in particular cattle and calves, contributes substantially to the ammonia emissions from the agricultural sector. Animal husbandry in Alberta represented 29% of the total Canadian emissions related to animal husbandry in 1980 and 25% in 1995. The ammonia emissions from animal husbandry are related to volatilization losses from manure in barns, storage facilities and from land spreading. According to EC (2000), quantification of this source of ammonia is difficult and estimates of the emissions are determined using loss rates, ammonia concentrations in manure and numbers of animals.

Table 7 **Ammonia Emissions to Air from Industrial Sources – Data for Canada and Alberta (EC, 2001a; EC, 2000; Geadah, 1985)**

Sector	Ammonia Emissions (tonnes)			
	Canada		Alberta	
	1980	1995	1980	1995
Industrial Sources	69,992	34,732	44,537	9,720
Aluminium Industry		229		
Asbestos Industry		4		
Cement and Concrete Industry		159		
Chemicals Industry	65,622[1]	20,782	43,820[1]	8,416
Ferrous Foundries		15		
Iron and Steel Industries		402		1
Iron Ore Mining Industry		24		
Mining and Rock Quarrying		228		104
Non-Ferrous Mining and Smelting Industry		300		
Oil Sands		766		766
Petrochemical Industry		182		
Petroleum Refining	3653	1,716	717	17
Pulp and Paper Industry		6,093		84
Wood Industry		1,739		2
Other Industries	718[2]	2,092		329
Non-industrial Fuel Combustion	1,496	2,930	99	579
Commercial Fuel Combustion		472		27
Electric Power Generation (Utilities)		1,015		483
Residential Fuel Combustion	1,496	616	99	36
Residential Fuel Wood Combustion		828		33
Transportation (Mobile Sources)	NA	19,693	NA	2,061
Incineration	306	471	7.5	24
Industrial and Commercial Incineration	102.2	136	7.5	
Municipal Incineration	188.9	65		
Wood Waste Incineration		196		24
Other Incineration and Utilities	15.3[3]	75		

[1] includes ammonia, ammonium nitrate, diammonium phosphate, sodium carbonate and urea production plants;

[2] refers to metallurgical coke manufacture emissions; 3 refers to incineration of sewage sludge; NA – not available

Table 8 Ammonia Emissions to Air from Agricultural Sources – Data for Canada and Alberta (EC, 2001a;EC, 2000; AAFC, 1998; Geadah, 1985)

Sector	Ammonia Air Emissions (tonnes)						
	Canada					Alberta	
	1980	1990[2]	1990[1]	1995[3]	1995[4]	1980	1995[4]
Animal Husbandry	**114,896**	**464,304**	**381,000**	**563,576**	**294,097**	**33,594**	**74,832**
Cattle and calves	108,078	257,383	211,000	331,016		32,614	
Hogs and pigs	6,293	92,439	76,000	106,822		851	
Sheep and lambs	525	2,468	2,000	2,492		129	
Poultry		107,388	88,000	107,388			
Horses		4,346	4,000	4,346			
Fur animals (mink and foxes)		279		279			
Fertilizer Application	**10,792**	**104,475**	**87,000**	**131,340**	**180,074[5]**	**4,767**	**50,443[5]**
Urea		86,081	71,000	109,232			
Ammonium sulphate		3,070	2,000	4,183			
Ammonium nitrate		2,292	2,000	2,1995			
Anhydrous ammonia	10,792	4,270	4,000	5,311		4,767	
Nitrogen solutions		1,975	2,000	1,981			
Monoammonium phosphate		4,565	6,000	4,948			
Diammonium phosphate		2,213		1,562			
Other phosphate fertilizers		9		0			
Other fertilizer materials		2		1925			

1 data from EC (2000); 2 data from AAFC (1998); 3 data from EC (2000); 4 data from EC (2001a); 5 these values include pesticide application and the growth and decomposition of fertilized agricultural crops

3.3 Other

Other emissions of ammonia include cigarette smoking (EC, 2001a; Geadah, 1985) and prescribed burning (EC, 2001a). According to Geadah (1985), cigarette smoking contributed 6 tonnes to ammonia emissions in Canada. Of this, 0.6 tonnes were attributed to Alberta. Environment Canada (2001a) reports slightly smaller ammonia emission values related to cigarette smoking for 1995: 5 tonnes for Canada and 0.4 tonnes for Alberta. Prescribed burning accounted for 303 tonnes of ammonia: 173 tonnes from Alberta (the largest contributor) and the rest from British Columbia, Ontario and Manitoba (EC, 2001a).

3.4 Ambient Ammonia Levels in Alberta

Table 9 summarizes the range of hourly maximum ambient ammonia concentrations reported on a monthly basis for several Alberta locations. Table 9 illustrates the greater variability in ammonia concentrations near industrial sources compared to that observed in community ambient air – in this case, in Fort Saskatchewan, Alberta. Fort Saskatchewan is the largest community in proximity to the Sherritt International Corp. facility in Alberta.

Additional recent data exist in the form of a survey of ambient air in proximity to feedlot operations in southern Alberta. Alberta Environment conducted an ambient air quality survey in the Counties of Lethbridge and Warner, Alberta (areas with intensive feedlot activities) for a period of ten days over four seasons between September 1998 and July 1999 (AENV, 2000b). The focus of the survey was to determine maximum impact of pollutants in ambient air downwind of feeding operations. Survey locations were very targeted in nature. One-hour average ammonia concentrations varied between 1 and 950 µg/m^3. (1.4 to 1,360 ppb). Control sites around the area – in the communities of Picture Butte, Stirling, and Lethbridge, Alberta – had concentrations ranging from 8 to 26 µg/m^3 (11 to 38 ppb).

Table 9 Range of Hourly Maximum Ammonia Concentrations at Selected Locations in Alberta

Ammonia Emission Source Location	Location of Monitor Relative to Source	Range of Hourly Maximum Concentration[1] $\mu g/m^3$ (ppb)	Period of Record
Agrium Products Inc. facility, Carseland, AB	1,200 m east of facility	14 to 4,110 (20 to 5,900)	Jan. 1990 to Nov. 2001
Agrium Inc. facility, Joffre, AB	800 m NW of facility	7 to 210 (10 to 300)	Jan. 1990 to Nov. 2001
Agrium Products Inc. facility, Redwater, AB	Fenceline	70 to 2,440 (100 to 3,500)	Jan. 1990 to Nov. 2001
Sherritt Int. Corp. facility, Fort Saskatchewan, AB	Location 1: fenceline	28 to 2,230 (40 to 3,200)	Jan. 1990 to Nov. 2001
	Location 2: fenceline	210 to 6,440 (300 to 9,240)	Jan. 1990 to Oct. 2001
	Location 3: 1,200 m southeast of facility	70 to 3,130 (100 to 4,500)	Jan. 1990 to Nov. 2001
Community of Fort Saskatchewan	Downtown: 9209A – 96 Ave.	7 to 370[2] (10 to 530)	Jan. 1995 to Dec. 2001

1 After Idriss (2002) unless otherwise noted

2 After CASA (2002)

4.0 EFFECTS ON HUMANS, ECOLOGICAL RECEPTORS AND MATERIALS

4.1 Humans and Animals

Ammonia is a volatile, highly water-soluble gas. The primary route of exposure to this chemical is via inhalation. The following summary focuses on the health effects of ammonia following inhalation by animals and humans. The most common effect of ammonia inhalation is irritation of the upper respiratory tract. Eye and skin irritation can also potentially occur at high air concentrations of ammonia.

The release of ammonia gas results in the formation of fine particulate matter ($PM^{2.5}$) through atmospheric reactions with common air pollutants. Epidemiological studies have positively associated $PM^{2.5}$ exposure with an increased incidence in respiratory disease and mortality. The human and ecological effects of $PM^{2.5}$ were not covered in this study.

4.1.1 Overview of Chemical Disposition

The following discussion of absorption, distribution, and excretion of ammonia following inhalation was based primarily on human studies (volunteer exposure to concentrations <500 ppm (348 mg/m^3)). One rat study involving higher exposure concentrations (up to 1,157 ppm (806 mg/m^3)) was also included. This allows some protection of the lower respiratory system. Human exposure studies have demonstrated that following short-term inhalation exposures of up to 500 ppm (348 mg/m^3) ammonia, approximately 80% of the inhaled ammonia is dissolved and absorbed in the mucous lining of the upper respiratory tract. Within thirty minutes the majority of absorbed ammonia is exhaled (ATSDR, 1990; US EPA, 1987; IPCS, 1986; NRC, 1979). Acute exposure to high ammonia concentrations (>500 ppm or 348 mg/m^3) or chronic exposure to relatively low concentrations, may saturate the scrubbing ability of the upper respiratory system, resulting in adverse effects on distal portions of the lung including chronic respiratory disease (Michaels, 1999; de la Hoz et. al., 1996). The adsorption of ammonia to dust also enables distribution to lower airways at concentrations not normally associated with an effect on the lower respiratory system (Donham et al., 2000; Kirkhorn and Garry, 2000).

No changes to blood or urinary nitrogen levels in exposed humans (<500 ppm)(<348 mg/m^3) indicate an insignificant absorption of ammonia into the bloodstream, and therefore, insignificant distribution to other body tissues. This is consistent with the toxic effects, which are predominately related to irritation or damage to upper respiratory tissues where absorption into mucous occurs (ATSDR, 1990;IPCS, 1986).

In rats, blood ammonia levels were unaffected by short-term inhalation of 32 ppm (22 mg/m^3) ammonia but significantly increased following exposure to 310 ppm (216 mg/m^3) to 1157 ppm (806 mg/m^3). When exposure was continued for 12 hours, blood levels returned to normal and remained so over the 24-hour treatment period, suggesting that an adaptive response mechanism may be activated with longer-term exposure (Schaerdel et al., 1983).

In humans and animals, exhalation is the primary route of excretion for inhaled ammonia (ATSDR, 1990).

4.1.2 Genotoxicity and Carcinogenicity

An increased frequency of chromosome aberrations and sister chromatid exchanges were reported for workers in a nitrogen fertilizer factory (Yadav and Kaushik, 1997). The ambient air concentration reported for ammonia was very low (0.1 ppm or 0.07 mg/m^3) and the potential for exposure to other nitroso compounds was not evaluated. In their review of ammonia toxicity, the ATSDR (1990) did not identify any data regarding genotoxic or carcinogenic effects following inhalation exposure of animals or human.

4.1.3 Acute Effects

Numerous studies have reported the acute adverse health effects of ammonia inhalation in animals and humans (Stombaugh et al., 1969; Coon et al., 1970; Mayan and Merilan, 1972; Richard et al., 1978; Tepper et al., 1985; IPCS, 1986; ATSDR, 1990; Urbain et al. 1996; Morgan, 1997; Murata and Horino, 1999; Jones et al., 2001; 2000).

The following discussion describes the effects from acute exposures of animals and humans as reported in selected studies published up until 2001. Tables 10 and 11 provide a summary of these effects in animals and humans, respectively.

The acute inhalation of ammonia can be severely debilitating or lethal to animals and humans at air concentrations greater than 5000 ppm (3483 mg/m^3), although very high air concentrations can be tolerated for short periods. In general, the acute health effects reported in animals following short-term inhalation of ammonia include: oral, nasal and eye irritation; respiratory tract irritation; decreased respiratory rate; increased respiratory depth; reduced body weight, and lethargy. The acute effects of ammonia inhalation by humans are similar to those reported in animal studies and include: oral, nasal and eye irritation, respiratory tract irritation, and increased respiratory depth.

4.1.3.1 Acute Adverse Health Effects in Experimental Animals

The lethal air concentration (LC50) for ammonia varies according to the species evaluated. One-hour LC50 values for ammonia range from up to 16,600 ppm (11,562 mg/m^3) for rats, 10,050 ppm (7,000 mg/m^3) for rabbits and cats and 4,837 ppm (3,369 mg/m^3) for mice. The duration of exposure also affects lethality, with very high concentrations tolerated over shorter or intermittent exposure periods (ATSDR, 1990; IPCS, 1986; Coon et al., 1970).

A pipeline rupture released a cloud of 99% anhydrous ammonia (no air concentration estimated) in a field of cattle resulting in death, spontaneous abortion, blindness and severe respiratory distress to cattle in the immediate vicinity of the leak. The symptoms reported in less severely exposed cattle included runny eyes, runny noses, coughing and wheezing (Morgan, 1997).

In rats, irritation of the upper respiratory tract and reduced body weight occurred following continuous exposure for 1 week to 500 ppm (348 mg/m^3) ammonia (Richard et al., 1978).

Lethargy (aversion to free-access wheel running) was reported in rats and mice exposed for 6 hours to 100 ppm (70 mg/m^3) ammonia (Tepper et al., 1985). A decrease in respiratory rate and an increase in respiratory depth were reported for rabbits exposed to 50 ppm (35 mg/m^3) ammonia over a 3-hour period (Mayan and Merilan, 1972).

Mild to moderate nasal irritation, ocular irritation (lacrimation) and dyspnea occurred in dogs and rabbits after 5 days of intermittent (8 hours a day) exposure to 770 mg/m^3 (1105 ppm) ammonia (Coon et al., 1970). These conditions disappeared upon the second week of exposure to the same concentration, suggesting an adaptation response. No irritation effects were reported for dogs and rabbits exposed to 155 mg/m^3 (223 ppm) ammonia over the same time period (Coon et al., 1970).

Exposure of pigs to 50 ppm (35 mg/m^3) ammonia over a 3 day period resulted in oral, nasal and ocular irritation, as well as coughing and a decrease in body weight. No adverse effects occurred in pigs exposed for the same duration to 10 ppm (7 mg/m^3) ammonia (Stombaugh et al., 1969).

Murata and Horino (1999) assessed the potential effects of ammonia on the respiratory system of cattle by exposing bovine lung neutrophils and bronchoalveolar macrophages *in vitro* to 50, 100 or 200 ppm (139 mg/m^3) ammonia over a one hour period. Bronchoalveolar macrophages were unaffected; however, ammonia concentrations as low as 50 ppm (35 mg/m^3) significantly affected lung neutrophils (*i.e.*, cell damage and inflammatory response), and resulted in a dose-dependent decrease in neutrophil recovery rates.

Based on evidence of changes in human olfactory sensitivity as a result of long-term exposure (5-32 years) to ammonia (30 ppm)(21 mg/m^3), Jones et al. (2001; 2000) tested the potential for ammonia to affect olfactory acuity in pigs. The acute exposure of pigs to 40 ppm (28 mg/m^3) ammonia (4 to 12 minutes over 4 consecutive days) did not compromise their ability to locate buried, odorized food. The short exposure periods (total of 16 or 48 minutes) may have been insufficient to elicit any effects on the olfactory system (Jones et al., 2000). Similarly, acute exposure (45 minutes) to 40 ppm (28 mg/m^3) ammonia did not affect the ability of pigs to perceive different concentrations of n-butanol. Olfactory effects from acute ammonia exposure are likely transient in nature as olfactory neurons are able to regenerate upon cessation of exposure (Jones et al., 2001).

In an investigation on the effects of ammonia exposure on the nasal and tracheal mucosa of pigs, Urbain et al. (1996) exposed piglets to 5 ppm (3 mg/m^3), 25 ppm (17 mg/m^3), 50 ppm (35 mg/m^3) or 100 ppm (70 mg/m^3) ammonia for 6 days. No clinical signs of exposure (*i.e.*, nasal discharge or sneezing) were reported, however, significant effects on nasal mucosa, (increased neutrophil count and epithelial hyperplasia) and functional disturbances of the tracheal smooth-muscle contractions, occurred at ammonia concentrations of 25 ppm (17 mg/m^3) or greater.

Table 10 Summary of Effects in Animals Following Acute Ammonia Exposure

Effects Reported	Exposure Period	Air Concentration (ppm (mg/m^3)[a])	Species	Reference
Respiratory irritation, decreased body weight and food uptake	1 wk 24 hr/d	500 (348)	Rat	Richard et al, 1978[b]
Lethargy	1 d 6 hr/d	100 (70)	Rat	Tepper et al., 1985[b]
Lethargy	1 d 6 hr/d	100 (70)	Mouse	Tepper et al., 1985[b]
Decreased respiratory rate, increased respiratory depth	1 d 3 hr/d	50 (35)	Rabbit	Mayan and Merilan, 1972[b]
No adverse effects	1 wk 5 d/wk 8 hr/d	223 (155)	Rabbit	Coon et al., 1970
Temporary dyspnea and lacrimation		1,105 (770)	Rabbit	
No adverse effects	1 wk 5 d/wk 8 hr/d	223 (155)	Dog	Coon et al., 1970
Temporary dyspnea and lacrimation		1,105 (770)	Dog	
No adverse effects	3 d	10 (7)	Pig	Stombaugh et al., 1969[b]
Oral, nasal and ocular irritation, coughing, decreased body weight and decreased food uptake		50 (35)	Pig	
No adverse effect on olfactory acuity	1 d 45 min	40 (28)	Pig	Jones et al., 2001; 2000
Increased neutrophil count of nasal mucosa and epithelial hyperplasia, functional disturbances of tracheal smooth-muscle contractions	6 d	25 (17)	Piglets	Urbain et al., 1996
Cell damage and inflammatory response of lung neutrophils, dose-dependent decrease in neutrophil recovery rates	1 hr	50 (35) (*in vitro* exposure)	Bovine lung neutrophils	Murata and Horino, 1999

[a] Conversion factor and assumptions used: mg/m^3 x 24.45/MW =ppm; MW=17.03, air at 25°C and 101.3 kPa (760mmHg) (Plog et al., 1996).

[b] Cited In: ATSDR (1990)

4.1.3.1.1 Infection Susceptibility

Animal studies have demonstrated that acute ammonia exposure can result in a decreased immune response and decreased resistance to bacterial infection in the development of respiratory disease (Hamilton et al., 1998; Targowski et al., 1984; Richard et al., 1978; Broderson et al., 1976). A significant decrease in immune response was reported for guinea pigs exposed to 90 ppm (63 mg/m^3) ammonia for 3 weeks prior to challenge with a derivative of tuberculin (Targowski et al., 1984). Mice continuously exposed for 1 week to 500 ppm (348 mg/m^3) ammonia exhibited a decreased resistance to infection of the respiratory tract by *Pasteurella multocida*. (Richard et al., 1978). Continuous exposure to 25 ppm (17 mg/m^3) ammonia for 4 weeks significantly increased the rate of infection and the severity of respiratory lesions in rats inoculated intranasally with *Mycoplasma pulmonis*, a bacteria responsible for murine respiratory mycoplasmosis (Richard et al., 1978; Broderson et al., 1976).

Recently, Hamilton et al. (1998) evaluated the synergistic role of ammonia exposure in the development of atrophic rhinitis in swine, a contagious disease of the upper respiratory tract primarily caused by colonization of the nasal cavity by *Pasteurella multocida*. Pigs inoculated with *P. multocida* and continuously exposed to 20 ppm (14 mg/m^3) ammonia over a 2 week period had significantly increased colonization of *P. multocida* organisms and clinical lesions in the nasal cavity compared to inoculated pigs not exposed to ammonia. The levels of ammonia in the nasal cavity mucus of exposed pigs were 7-fold higher than unexposed pigs. Upon cessation of ammonia exposure, the number of *P. multocida* colonies rapidly declined, allowing for recovery of normal flora.

4.1.3.2 Acute Adverse Health Effects in Humans

The ATSDR (1990) has cited a lethal ammonia dose of 5000 ppm (3483 mg/m^3) for humans exposed for 30 minutes (Henderson and Haggard, 1927). Michaels (1999) identified a zero mortality concentration of 33,737 ppm (23,499 mg/m^3) ammonia for a 5 minute exposure period, based on a detailed analysis of data on accidental releases of ammonia and subsequent effects on workers. Fatality from acute ammonia inhalation usually results from severe laryngeal edema and obstruction, pulmonary edema, or extensive pneumonic complications; necropsy findings have also reported cerebral hemorrhage and severe liver damage (Darchy et al., 1997; de la Hoz et al., 1996; NRC, 1979)

4.1.3.2.1 Accidental Human Exposures

Chronic relapsing sinusitis was reported in an individual exposed to ammonia fumes as a result of a train spill (Brautbar, 1998). Ammonia exposure occurred for several hours and air concentrations were estimated to be well above those associated with severe nasal irritation (i.e., > 100 ppm or 70 mg/m^3).

Severe chemical burns and inhalation injury occurred in an individual acutely exposed to very high concentrations of anhydrous ammonia gas, following an explosion at a fertilizer factory. The necrotic effects on the lungs (bleeding of the respiratory tract, inflammation of the pharynx) and skin (second and third degree burns) were attributed to ammonium hydroxide, a product of ammonia and water. The authors cite previous work attributing skin damage as a result of exposure to ammonia air concentrations of 10,000 ppm (6965 mg/m^3) or greater (Amshel et al., 2000).

Three individuals that were acutely exposed to very high concentrations of ammonia (no measured values) as a result of leaks or spills, were evaluated 2 years following the exposure event (de la Hoz et al., 1996). All three complained of persistent respiratory symptoms and were diagnosed with chronic lung disease (i.e., chronic dyspnea, restrictive lung dysfunction, obstructive lung disease, bronchial hyper-reactivity and small airway disease) as a result of the exposure.

4.1.3.2.2 Controlled Human Exposures

Sixteen volunteers were exposed for a 2 hour period to 50 ppm (35 mg/m^3), 80 ppm (56 mg/m^3), 110 ppm (77 mg/m^3) or 140 ppm (98 mg/m^3) ammonia (Verberk, 1977). Pulmonary function tests were performed before and after ammonia exposure. Significant eye and throat irritation were reported by volunteers exposed to concentrations greater than 50 ppm (35 mg/m^3) (80-140 ppm)(56-98 mg/m^3), some volunteers were unable to tolerate 140 ppm (98 mg/m^3) ammonia for the full 2 hours. There were no measurable effects on pulmonary function in any of the exposed groups.

Volunteers exposed to 500 ppm (348 mg/m^3) ammonia for 30 minutes experienced nasal and throat irritation as well as increased respiratory minute volume (Silverman et al., 1949). Individuals exposed to 100 ppm (70 mg/m^3) ammonia for 6 weeks (6 hours a day, 5 days a week,) experienced irritation of the eyes, nose and throat during the first week of exposure, ammonia tolerance appeared to develop afterwards. No adverse respiratory effects or eye irritation were reported following exposure to 50 ppm (35 mg/m^3) ammonia over the same time period (Ferguson et al., 1977).

Cormier et al. (1997) reported acute respiratory effects (inflammatory response, acute respiratory symptoms and an increase in bronchial responsiveness) in 7 previously unexposed subjects following two 5-hour exposure periods (8 days apart) in a swine confinement building environment. Exposure to ammonia and total dust were measured by personal sampling. The mean exposure concentrations (5 hour time weighted average (TWA)) for all subjects over the two periods were 10.1 mg/m^3 (14.5 ppm) and 12.4 mg/m^3 (17.8 ppm) for ammonia and 8.5 and 17 mg/m^3 for total dust. A more intense inflammatory response in previously unexposed subjects compared to chronically exposed workers suggests either a healthy worker selection process or adaptation to the environment.

4.1.4 Chronic Effects

The effects of chronic ammonia exposure in animals and humans are described below. These effects are summarized in Tables 12 and 13 for animals and humans, respectively.

In general, the health effects following chronic exposure of animals to ammonia via inhalation include: nasal irritation; inflammatory response in lungs; reduced olfactory acuity, and lethargy. Animal studies have also demonstrated that ammonia exposure reduces immune response and

Table 11 Summary of Effects in Humans Following Acute Ammonia Exposure

Effects Reported	Exposure Period	Air Concentration (ppm (mg/m^3)[a])	Reference
Death	30 min	5,000 (3,483)	Henderson and Haggard, 1927[b]
Nasal and throat irritation, increased minute volume	1 d 30 min	500 (348)	Silverman et al., 1949[b]
No adverse effect	1 d 2 hr/d	50 (35)	Verberk, 1977
Coughing, eyes, nose and throat irritation	1 d 2 hr/d	80 / (56)	Verberk, 1977
No adverse respiratory effects or eye irritation	6 wk 5 d/wk 6 hr/d	50 / (35) 100 (70)	Ferguson et al., 1977[b]
Transient irritation of eyes, nose and throat			
Inflammatory response, acute respiratory symptoms and an increase in bronchial responsiveness	2 d 5 hr/d (8 days apart)	14.5 (10.1)	Cormier et al, 1997

[a] Conversion factor and assumptions used: mg/m^3 x 24.45/MW =ppm; MW=17.03, air at 25°C and 101.3 kPa (760mmHg) (Plog et al., 1996).

[b] Cited In: ATSDR (1990)

increases susceptibility to bacterial infection of the respiratory tract. Chronic effects reported in humans include: reduction in pulmonary function; cough; phlegm; wheeze, and dyspnea.

4.1.4.1 Chronic Adverse Health Effects in Animals

Coon et al. (1970) performed an extensive evaluation of the effects of repeated or continuous ammonia exposure in a variety of animal species (rats, guinea pigs, rabbits, dogs, and monkeys). Rats, guinea pigs, rabbits, dogs and monkeys were repeatedly exposed to 155 mg/m^3 (223 ppm) or 770 mg/m^3 (1105 ppm) ammonia for 8 hours a day, 5 days a week, over a 6-week period. An increased incidence of nonspecific inflammatory changes occurred in the lungs of rats and guinea pigs repeatedly exposed to 770 mg/m^3 (1105 ppm). Focal pneumonitis developed in the lung of 1 of the 3 exposed monkeys following repeated exposures to 155 mg/m^3 (223 ppm) ammonia.

No significant effects were reported in rats, guinea pigs, rabbits, dogs and monkeys continuously exposed to 50 ppm (35 mg/m^3) ammonia for 114 days. Lipid filled macrophages were observed in the lungs of 2/2 exposed dogs, 1/3 monkeys and 1/15 rats (Coon et al., 1970).

Rats were continuously exposed for 90 days to ammonia at concentrations of 127 mg/m^3 (182 ppm), 262 mg/m^3 (376 ppm), 455 mg/m^3 (653 ppm), or 470 mg/m^3 (675 ppm) (Coon et al., 1970). Nonspecific inflammatory changes in the lungs and kidneys were observed at 127 mg/m^3 (182 ppm), mild nasal discharge, as well as nonspecific circulatory and degenerative changes in lungs and kidneys occurred in rats exposed to 262 mg/m^3 (376 ppm). Continuous exposure to

455 mg/m^3 (653 ppm) and 470 mg/m^3 (675 ppm) resulted in a high incidence of mortality (50/51 rats and 13/15 rats, respectively) with all of the exposed animals demonstrating nasal irritation and dyspnea (Coon et al., 1970).

Guinea pigs, rabbits, dogs and monkeys were continuously exposed to 470 mg/m^3 (675 ppm) ammonia for 90 days (Coon et al., 1970). Effects reported included: death (4/15 guinea pigs); eye irritation (dogs and rabbits), nasal discharge (dogs); lung congestion (rabbits); focal or diffuse interstitial pneumonitis (all animals), and an increased calcification of renal tubular and bronchial epithelia, proliferation of renal tubular epithelium, myocardial fibrosis and fatty changes of liver plate cells (several animals of each species) (Coon et al., 1970).

Broderson et al. (1976) reported lesions and epithelial hyperplasia in the nasal passages of rats continuously exposed to 150 ppm (104 mg/m^3) ammonia (from soiled bedding) over a 75 day exposure period, or exposed to 250 ppm (174 mg/m^3) purified ammonia 3 hours a day, for 35 days.

No adverse effects were reported in pigs continuously exposed to 50 ppm (35 mg/m^3) ammonia for four weeks; however, lethargy occurred in pigs exposed over the same period to 100 ppm (70 mg/m^3) ammonia (Drummond et al., 1980). Continuous exposure to 40 ppm (28 mg/m^3) ammonia over a 24 day period significantly reduced pigs olfactory acuity, as measured by the perception of n-butanol concentrations. Removal of the affected pigs to fresh air for 24 days resulted in only partial recovery of acuity in one pig and no recovery in the other two affected animals. The authors suggest that olfactory perception was altered due to inflammation and damage to nasal epithelium and damage/over stimulation of the olfactory receptors. It was also postulated that a longer exposure period would likely have increased the damage to olfactory acuity (Jones et al., 2001).

4.1.4.2 Chronic Adverse Health Effects in Humans

4.1.4.2.1 Industrial Exposures

No significant effects on measured pulmonary function were identified in soda ash workers chronically exposed to mean airborne ammonia concentrations of 9.2 ppm (6 mg/m^3) (Holness et al., 1989). No associations were made between changes in lung function and ammonia concentration or length of exposure. The prevalence of self-reported symptoms (respiratory, eye and skin) was similar for unexposed controls and exposed workers, although exposure to ammonia was reported to aggravate symptoms (*i.e.*, cough, wheeze, nasal complaints, eye irritation and sore throat) in workers. There was no significant difference in odor detection between exposed workers and unexposed controls (Holness et al., 1989).

Zlatev et al. (1998) conducted biomonitoring of workers producing ammonia in a nitrogen fertilizer plant. Workers were exposed to mean shift ammonia concentrations ranging from 1.5 to 7.5 times higher than the recommended TLV (25 ppm/17 mg/m^3). A statistically significant relationship was found between biochemical parameters of workers (measured in blood and urine) and ammonia exposure. Occupational exposure was positively associated with disturbances in the metabolism of nitrogen and minerals and disturbances in hepatic function.

Table 12 Summary of Effects in Animals Following Chronic Ammonia Exposure

Effects Reported	Exposure Period	Air Concentration (ppm (mg/m^3)^a	Species	Reference
Mild nasal discharge, non-specific circulatory and degenerative changes in lungs and kidneys	90 d	376 (262)	Rat	Coon et al., 1970
Nasal lesions, epithelial hyperplasia	75 d 24 hr/d	150 (104)	Rat	Broderson et al., 1976
Non-specific inflammatory changes in lungs	6 wk 5 d/wk 8 hr/d	1,105 (770)	Rat	Coon et al., 1970
No adverse effects	114 d	57 (40)	Guinea pig	Coon et al., 1970
Non-specific inflammatory changes in lungs	6 wk 5 d/wk 8 hr/d	1,105 (770)	Guinea pig	Coon et al., 1970
No adverse effects	4 wk	50 (35)	Pig	Drummond et al., 1980^b
Lethargy		100 (70)		
No adverse effects	6 wk 5 d/wk 8 hr/d	1,105 (770)	Dog	Coon et al., 1970
No adverse effects	114 d	57 (40)	Rabbit	Coon et al., 1970
Focal pneumonitis	6 wk 5 hr/wk 8 hr/d	223 (155)	Monkey	Coon et al., 1970
Reduced olfactory acuity	24 d	40 (28)	Pig	Jones et al., 2001

[a] Conversion factor and assumptions used: mg/m^3 x 24.45/MW =ppm; MW=17.03, air at 25°C and 101.3 kPa (760mmHg) (Plog et al., 1996).

[b] Cited In: ATSDR (1990)

Pulmonary function tests were carried out on ammonia plant workers and administrative staff (Ali et al., 2001). Measured ammonia concentrations in the plant ranged from 3 ppm (2 mg/m^3) to 186 ppm (130 mg/m^3), with 30% of the air samples above the recommended TLV (25 ppm)(17 mg/m^3). Cumulative ammonia exposures were estimated and plant workers were divided into 2 groups based on predicted exposure level and duration of exposure (greater or less than 50 mg/m3-years (72 ppm-years). Significant reductions in forced expiratory volume (FEV$_1$ % predicted) and in forced vital capacity (FVC % predicted) were determined for workers in the group chronically exposed to greater than 72 ppm-years. Self-reported chronic respiratory symptoms of these workers included cough, phlegm, wheeze or dyspnea (Ali et al., 2001).

4.1.4.2.2 Agricultural Exposures

Ammonia is a breakdown product of urea in animal urine. The intense confinement of poultry and swine in the agricultural industry has resulted in respiratory illness in workers occupationally exposed to ammonia as well as endotoxin (cell membrane component of coliform bacteria), respirable dust, and other gases resulting from the bacterial conversion of animal waste products (hydrogen sulphide, carbon dioxide and methane) (NRC, 1979; Reynolds et al., 1996; Vogelzang et al., 1997; Kirkhorn and Garry, 2000; Donham et al., 2000). Some of the respiratory disorders reported in workers in swine and poultry confinement buildings include: acute lower respiratory tract inflammation, cough, dyspnea, chest tightness, and chronic bronchitis (Von Essen and Donham, 1999).

Reynolds et al. (1996) conducted a study on swine production workers exposed to ammonia, endotoxin, and dust (respirable and total). A significant dose-response relationship was determined between exposure and decrements in pulmonary function measured pre- and post-shift. Threshold values associated with a 2% decline in forced expiratory volume over 1 second (FEV_1) were 7.5 ppm (5 mg/m^3) for ammonia, 2.5 mg/m^3 for total dust.

Vogelzang et al. (1997) evaluated the hyper-responsiveness of bronchial mucosa in pig farmers with and without chronic respiratory symptoms (*i.e.*, cough, phlegm, shortness of breath, wheezing, and chest tightness). Personal exposures to ammonia and respirable dust (including endotoxin) were measured in summer and winter. The geometric mean air concentrations (8-hour TWA) across all farmers evaluated was 1.7 mg/m^3 (2.4 ppm) for ammonia, 2.7 mg/m^3 for respirable dust, and 111 ng/m^3 for endotoxin. Mild bronchial hyper responsiveness was associated with several farm techniques (*i.e.*, the use of quaternary ammonium compounds as disinfectant, wood shavings as bedding, automated dry feeding, pellet feed and the location of air exhaust). The study did not, however, find a significant association between measured exposure to ammonia, dust or endotoxin and measured bronchial responsiveness. In addition, there was no significant difference between exposure of symptomatic versus asymptomatic farmers to ammonia, dust and endotoxin

Donham et al. (2000) conducted a study of poultry workers exposed to ammonia, endotoxin, and dust (respirable and total). A significant dose-response relationship was determined between exposure and decrements in pulmonary function measured pre- and post-shift. The threshold values associated with a 3% decline in forced expiratory volume over 1 second (FEV_1) were 12 ppm (8 mg/m^3) for ammonia, 2.4 mg/m^3 for total dust, 0.16 mg/m^3 for respirable dust and 614 EU/m^3 for endotoxin.

Ammonia gas is normally absorbed by mucous membranes of the upper airways at ambient air concentrations, however, once adsorbed to respirable dust, ammonia can penetrate deeper into the lungs, increasing the risk of illness in the lower respiratory tract at low ammonia concentrations. In their review of agricultural lung disease, Kirkhorn and Garry (2000) argue that current occupational limits for ammonia (25 to 50 ppm)(17 mg/m^3 to 35 mg/m^3) are not appropriate for animal confinement workers, and recommend an ammonia limit of 7.5 ppm (5 mg/m^3), based on the work of Reynold et al. (1996). In addition to occupational risks, the authors raise concerns of respiratory health issues in areas neighboring animal confinement facilities (Kirkhorn and Garry, 2000).

4.1.4.2.3 Ambient Air Exposures

Zuidema and Nentjes (1997) reported a positive and significant relationship between ammonia air concentrations in the Netherlands (1987-1989) and the number of work loss days caused by respiratory illness (chronic bronchitis, asthma and chronic non-specific lung disease). Ambient air concentrations of ammonia were reported to range from 320 to 1190 mol/ha.

Gomzi and Saric (1997) evaluated the effects of continuous exposure to low levels of pollution on the respiratory system of children (8-9 years old). The study was conducted over a 6-month period, during which the incidence of acute respiratory disease in children living and attending school in an area with a fertilizer plant was compared with children in a "control" area with no specific industrial source. Forced expiratory volumes (FEV) were determined at the beginning and end of the study. Ammonia, hydrogen fluoride, nitrogen dioxide, total suspended particulate and smoke were measured (24-hour sampling) in ambient air and inside schools throughout the study. In the vicinity of the fertilizer plant, mean ambient ammonia concentrations ranged from 54 $\mu g/m^3$ (0.08 ppm) to 113 $\mu g/m^3$ (0.16 ppm), with a maximum value of 699 $\mu g/m^3$ (1.0 ppm). Inside the school, ammonia concentrations ranged from 117 $\mu g/m^3$ (0.17 ppm) to 161 $\mu g/m^3$ (0.23 ppm), with a maximum value of 423 $\mu g/m^3$ (0.61 ppm). In the control area, mean ambient ammonia concentrations ranged from 30 $\mu g/m^3$ (0.04 ppm) to 63 $\mu g/m^3$ (0.09 ppm), with a maximum value of 152 $\mu g/m^3$ (0.22 ppm). Inside the school, mean concentrations ranged from 98 $\mu g/m^3$ (0.14 ppm) to 102 $\mu g/m^3$ (0.15 ppm), with a maximum value of 231 $\mu g/m^3$ (0.33 ppm). There was no significant difference in measured FEV between the groups of children, however, the rate of reported acute respiratory disease was significantly greater for children in the vicinity of the fertilizer plant compared to the control area.

In a similar study, Gomzi, (1999) evaluated respiratory effects in children (8-10 years old) exposed to nitrogen dioxide, ammonia, particulate matter and parental tobacco smoke. Ambient air and indoor school air were monitored at an industrial location and a rural location. The study was conducted over a 6-month period during which the incidence of acute respiratory disease was recorded. At the industrial site, the mean ambient ammonia concentrations ranged from 54 $\mu g/m^3$ (0.08 ppm) to 82 $\mu g/m^3$ (0.12 ppm), with a maximum value of 422 $\mu g/m^3$ (0.61 ppm). Inside the school, mean concentrations ranged from 121 $\mu g/m^3$ (0.17ppm) to 161 $\mu g/m^3$ (0.23 ppm), with a maximum 423 $\mu g/m^3$ (0.61 ppm). At the rural site, mean ambient ammonia concentrations ranged from 30 $\mu g/m^3$ (0.04 ppm) to 63 $\mu g/m^3$ (0.09 ppm) (maximum value of 152 $\mu g/m^3$ or 0.22 ppm). Inside the rural school, mean ammonia concentrations ranged from 98 $\mu g/m^3$ (0.14 ppm) to 102 $\mu g/m^3$ (0.15 ppm) (maximum value of 231 $\mu g/m^3$ or 0.33ppm). This study did not find a statistically significant difference in the prevalence of reported acute respiratory illness between children from the industrial versus rural location.

Turnovska et al. (1998) evaluated the respiratory function of children (mean age 10.4 years) attending 3 schools located at various distances from industrial sources of air pollution. Mean annual ambient air concentrations of ammonia, hydrogen sulphide, nitrogen dioxide, particulate matter and sulphur dioxide were measured at 3 stations in the vicinity of 3 schools. School #1 was located in close proximity to fertilizer and steam (brown coal fuel) plants, school #2 was located near an asbestos-cement plant and school #3 was located 4 to 7 kilometers away from these industrial sources. The mean annual ammonia concentrations were 69 $\mu g/m^3$ (0.10 ppm) for school #1, 165 $\mu g/m^3$ (0.24 ppm) for school #2 and 69 $\mu g/m^3$ (0.10 ppm) for school #3. Respiratory function of the children was evaluated by a comprehensive functional investigation of breathing. There was no significant difference in ammonia ambient air concentrations between the 3 sites and subsequently, no significant difference in lung function parameters for the children exposed at the 3 sites.

4.1.5 Summary Of Adverse Health Effects Of Ammonia Inhalation

The results of acute inhalation exposure studies conducted in animals and humans all indicate that ammonia is primarily an irritant of the upper respiratory tract. Animal studies detected subtle responses at air concentrations where earlier studies did not report any effects (*i.e.*, no effects observed in pigs exposed to 50 ppm (35 mg/m^3) for 4 weeks (Drummond et al, 1980) versus reduced olfactory acuity in pigs exposed for 24 hours to 40 ppm (28 mg/m^3) (Jones et al., 2001)).

The effects reported at mean exposure concentrations (time-weighted average) do not provide information regarding potential short-term peaks in exposure concentrations. The work of de la Hoz et al. (1996) indicates that acute exposure to very high concentrations of ammonia led to chronic lung disease years after initial exposure. No studies were identified which evaluated the chronic effects following acute exposure to moderately high concentrations.

An ammonia air concentration of 9.2 ppm (6 mg/m^3) did not result in adverse health effects in industrial workers (Holness et. al., 1989). The adsorption of ammonia to fine dust allows for distribution to lower airways at gaseous ammonia concentrations not normally associated with an effect of the lower respiratory system (Kirkhorn and Garry, 2000; Donham et al., 2000; Reynolds et. al., 1996). Gomzi and Saric (1997) found a significant increase in the rate of reported acute respiratory disease in children exposed to ambient air concentrations of ammonia up to a maximum of 1 ppm (0.7 mg/m^3), when compared to a control group exposed to a maximum of 0.22 ppm (0.15 mg/m^3) ammonia.

The majority of chronic human exposure studies are related to industrial and agricultural exposures where multiple chemical exposures can confound the effects attributable to one chemical. In addition, human exposure studies based on occupational exposures typically involve "healthy workers" and do not include sensitive individuals (*i.e.*, children, elderly) who may be adversely affected at lower air concentrations of ammonia.

4.2 Vegetation

Ammonia may affect vegetation by influencing the nitrogen cycling in ecosystems (Fangmeier et al. 1994). Depending on the sensitivity of vegetation, exposure to ammonia may be directly harmful to plants. This section provides a summary of an extensive literature review on the effects of ammonia exposure on vegetation by Krupa (2002). The reader is referred to Krupa (2002) for additional information.

Table 13 Summary of Chronic Effects in Human Subjects Following Inhalation Exposure to Ammonia

Effects Reported	Exposure Period	Air Concentration ppm (mg/m^3)^a	Reference
No adverse effects on lung function	12.2 yr	9.2 (6) (mean occupational exposure)	Holness et al., 1989
Reduction in pulmonary function of exposed workers (FEV$_1$, (FVC); self-reported chronic respiratory symptoms (cough, phlegm, wheeze or dyspnea)	> 1 yr	> 72 ppm-years (50 mg/m^3-years) (estimated cumulative occupational exposure)	Ali et al., 2001
Significant increase in the incidence of reported acute respiratory disease in children	> 6 mo.	Mean range ambient air: 0.08 to 0.16 (0.054 to 0.113) (max 1.0 (0.699)) School air: 0.17 to 0.23 (0.117 to 0.161) (max 0.61 (0.423))	Gomzi and Saric, 1997
No increase in the reported incidence of acute respiratory disease in children	> 6 mo.	Mean range ambient air: 0.08 to 0.12 (0.054 to 0.082) (max 0.61 (0.422)) School air: 0.17 to 0.23 (0.121 to 0.161) (max: 0.61 (0.423))	Gomzi, 1999
3% decline in FEV$_1$ measured pre- and post-shift	9.7 yr	12 (8) (mean occupational exposure)	Donham et al., 2000
2% decline in FEV$_1$ measured pre- and post-shift	10.7 yr	7.5 (5) (mean occupational exposure)	Reynolds et al., 1996
No significant association between ammonia exposure and measured bronchial responsiveness	15.1 yr	2.5 (1.7) (mean occupational exposure)	Vogelzang et al, 1997

[a] Conversion factor and assumptions used: mg/m^3 x 24.45/MW =ppm; MW=17.03, air at 25°C and 101.3 kPa (760mmHg) (Plog et al., 1996).

4.2.1 Effects of NH_3 and NH_4^+ (NH_y) on Vegetation

Both anthropogenic NH_3 and NH_4^+ derived from it, significantly influence nitrogen cycling in ecosystems (Krupa, 2002). Since under field conditions the chronic effects of NH_3 and NH_4^+ are often difficult to distinguish, the two are considered together as NH_y.

Fangmeier et al. (1994) provided a state of the science review of the effects of NH_y on plants. The current knowledge of the effects of NH_y on plants is based on studies using a number of different approaches. These include experimental designs using artificial exposures to NH_3 or NH_4^+ either in controlled environment chambers, greenhouses, closed or open-top field chambers and chamber-less field studies where the physical and the chemical (pollution) climate are not controlled. For details on various exposure methods, the reader is referred to Manning & Krupa (1992). Fangmeier et al. (1994) and Krupa (2002) provided a summary of studies published within the past 20 years about the effects of NH_3 on plants. According to Fangmeier et al. (1994), NH_y effects on plants depend on several processes:

- uptake
- detoxification/assimilation
- development of injury when the amount of uptake exceeds detoxification
- metabolic changes related to detoxification/assimilation
- secondary effects following NH_y uptake and successful detoxification

4.2.1.1 Uptake of NH_y by Shoots and Roots

NH_3 (shoots): Atmospheric NH_3 enters the leaves of higher plants almost exclusively through the stomata and is dissolved in the water film of the mesophyll cells to form NH_4^+ (Van Hove et al., 1987). The driving force for NH_3 uptake is its concentration gradient between ambient air and the mesophyll tissue. As long as the ambient NH_3 concentration exceeds the mesophyll concentration (compensation point), NH_3 uptake by the shoot will occur.

NH_4^+ (shoots): NH_4^+ is accumulated on leaf surfaces both by dry and wet deposition (Gmur et al., 1983; Van Hove et al., 1989; Bobbink et al., 1992a). The question of how NH_4^+ enters the leaves has not yet fully been answered. Wilson (1992) concluded that uptake was due to diffusion rather than H^+ or base cation exchange as commonly accepted. That conclusion should be tempered, because as opposed to solutions or precipitation, fine particle (size < 2.5 µm) deposition of NH_4^+ follows Brownian motion and not diffusion. Nevertheless, fine particles enter the leaf through stomata, in the same way as NH_3 (Chevone et al., 1986).

NH_y (roots): Normally root uptake of NH_3 does not occur since the NH_3 deposited to the soil is readily dissolved to yield NH_4^+. NH_4^+ in soils is less mobile than NO_3^-, but is easily accessible to plants under most conditions (Brady, 1990). Uptake of NH_4^+ leads to acidification of the rooting zone, since it is exchanged with protons exuded by the roots (Tamm, 1991). Another problem arises from competition in the uptake between NH_4^+ and other cations such as K^+ (Lips et al., 1987; Vale et al., 1987). K^+ deficiency may occur in plants provided with NH_4^+ as sole N-source (Kinzel, 1982; Roelofs et al., 1985). However, NH_4^+ uptake via the roots may be reduced if shoot uptake of NH_y occurs. Pérez-Soba and Van der Eerden (1993) found decreased NH_4^+ sorption in roots of *Pinus sylvestris* (Scotch pine) when the shoots were fumigated with NH_3.

4.2.1.2 Assimilation and Detoxification of NH_y.

NH_3 taken up by the shoots readily reaches equilibrium with NH_4^+ in the water film of the mesophyll tissue. There, NH_4^+ strongly dominates NH_3 and is assimilated, whereas NH_4^+ taken up from the soil is metabolized in the roots. Both in the roots and in the shoots, NH_4^+ assimilation takes place via the enzymes glutamine synthetase/glutamate synthase (GS/GOGAT) system (Lewis et al. 1987; Stewart et al. 1987; Wallsgrove, 1987).

4.2.1.3 Metabolic Changes Due to NH_y Assimilation and Detoxification

NH_y detoxification may lead to significantly increased contents of organic nitrogen. If NH_y uptake exceeds the assimilation capacity, NH_y will accumulate in the tissue resulting in toxic effects (Fangmeier et al. 1994). Tissue accumulation of NH_y was observed in lettuce (*Lactuca sativa* var. *capitata*) and tomato following exposures to acute NH_3 concentrations, in controlled conditions (Van der Eerden, 1982; Hülsenberg, 1990) and in highly polluted conifer stands near livestock farms (Tesche and Schmidtchen, 1978; Heinsdorf and Krauß, 1991).

4.2.1.4 Changes in Leaf Gas Exchange Following Exposure to NHy.

NH_3 uptake may cause an autocatalytic increase of further NH_3 flux into the leaves by inducing stomatal opening via the internal CO_2 level, as long as photon flux density is sufficient for equivalent photosynthesis (Van der Eerden and Pérez-Soba, 1992).

4.2.1.5 Effects of NHy on Epicuticular Waxes

NH_y entering the leaves via the stomata may affect mesophyll processes and may also directly alter the cuticle. Although experimental results show that NH_y can damage the epicuticular wax layer, that effect is difficult to assess under field conditions, because of natural fluctuations in growth, aging, wax re-crystallization, presence of other air pollutants and stress factors and high intra-species variation (Krupa, 2002). Needles of *Pseudotsuga menziesii* (Douglas fir) exposed to NH_3 in climate controlled growth chambers (Van der Eerden et al., 1992), in open-top chambers (Thijse and Baas, 1990) and tree stands polluted with NH_y (Thijse and Baas, 1990) showed erosion of the crystalline wax structures. Erosion also occurs naturally during needle aging, however, it was enhanced by NH_3 in the experiments. In contrast, no significant effects were found on wax erosion (e.g., building of amorphous wax) in *Pinus sylvestris* needles exposed to NH_3 at 60 or 100 $\mu g/m^3$ (86 or 144 ppb) for nine months (Bacic et al., 1992) or in *Populus euramericana* leaves fumigated for seven weeks at 64 $\mu g/m^3$ (92 ppb) (Van Hove et al., 1991).

4.2.1.6 Factors Determining the Toxicity of NH_y

A number of internal and external factors determine the toxicity of NH_y. Internally, NH_y may: (a) function as an electron acceptor, thus causing uncoupling of electron transport along membranes (Losada and Arnon, 1963); (b) saturate membrane lipids, thus causing membrane dysfunction (Van der Eerden, 1982) and (c) cause direct leaf etching and necrosis (death) at very high concentrations (Van der Eerden et al., 1990). Since NH_y may not be stored in the tissues without damage, plants readily try to assimilate NH_y to form organic nitrogen compounds. Thus, primary toxicity of NH_y arises as soon as uptake exceeds assimilation capacity.

Externally, environmental conditions such as irradiation, temperature and moisture availability influence the toxicity of NH_y. NH_y is more toxic under conditions limiting photosynthetic capacity and thus, availability of carbon skeletons and energy (Van der Eerden, 1982).

4.2.1.7 Direct Toxicity of NH_y and Visible Foliar Injury

Accidental releases of NH_3 from industrial processes or during transport are known. In most of these cases, the concentrations will be extremely high and the exposure time will be very short. In these episodes the dominant cause of injury is a direct chemical 'etching' of the foliage (Temple et al., 1979; De Temmerman, 1980).

Generally, the assimilation capacity of a plant species determines the degree of injury. If the assimilation capacity is not sufficiently high to detoxify NH_y, acute (visible) injuries may occur. On broad-leafed plants acute exposures to anhydrous NH_3 will result in the death of the leaf tissue between the veins (interveinal necrosis) (Krupa, 2002). This can be easily confused with similar symptoms caused by acute exposures to sulphur dioxide (SO_2) (Krupa and Legge, 1999). Conifers near livestock farms usually respond to NH_3 by needle necrosis (death) starting at the tips of the oldest needles, subsequently with needle loss and finally with the death of the tree. In the former GDR (East Germany), in the vicinity of huge pig farms with up to 200,000 pigs, forest decline areas of 2,000 ha attributable to NH_3 have been observed (Hofmann and Heinsdorf, 1990).

4.2.2 Secondary Effects of NH_y Uptake and Assimilation on Vegetation

4.2.2.1 Growth Responses

One of the most obvious plant responses that might be regarded as the 'secondary' effect after NH_y assimilation, is enhanced growth (Fangmeier et al. 1994). This should not be surprising since nitrogen must be regarded as a limiting factor (in the sense of biomass production) for plant growth in most (natural) habitats. Enhanced growth has been observed in many experiments as long as the NH_y concentrations were not toxic. At acute (toxic) NH_3 concentrations, however, growth is depressed (Van Haut et al., 1979; Van der Eerden, 1982; Hülsenberg, 1990). Whenever increased growth is observed after NH_y application, it is mainly due to the shoot growth response. Root growth increases only a little or at least less than shoot growth, leading to higher shoot/root ratios (Encke, 1986).

Enhanced growth caused by NH_y uptake may not necessarily be regarded as beneficial but rather as detrimental, if other effects such as decreased resistance to environmental stress as described in the following section are considered. Some experimental findings indicate that growth enhancement may turn into increased mortality of plants at a later developmental stage or during environmental stress.

4.2.2.2 Resistance to Stress

Drought and frost resistance: Studies have indicated that NH_y may decrease the resistance to drought stress and reduce frost hardiness (Fangmeier et al. 1994; Krupa, 2002).

Decrease in the resistance to drought stress by NH_y may be explained by at least two mechanisms. First, the demand for carbon skeletons to assimilate NH_y increases CO_2 uptake and thus, stomatal opening and water loss. Secondly, since shoot growth is more enhanced by NH_y

than root growth, water supply from the roots may easily become insufficient during periods of drought (Fangmeier et al. 1994).

Regarding frost hardiness, Dueck et al. (1990) believe that NH_3 at low to moderate concentrations prolongs the growth phase in autumn and causes winter hardiness to develop too late, with detrimental consequences if first frost periods occur early in the year.

Weakening of defense against pests: Most insect pests may attack their hosts more successfully at nitrogen levels in the host tissue higher than those usually found under field conditions. Increased nitrogen content caused by NH_y uptake may thus weaken the host defense against pests (Fangmeier et al. 1994). In addition, altered foliar C:N ratios and altered allelo-chemicals in the plant may influence herbivory, as with N fertilization (Krupa et al. 1998).

Pathogens: Several field observations indicate that trees are more susceptible to fungal infection under high nitrogen status (irrespective of the form and path of nitrogen enrichment, i.e. NH_y or NO_x, fertilizer application or atmospheric deposition) or altered nutrient balance such as increased N/K ratios (Ylimartimo, 1991). Vasander and Lindholm (1985) suggest that N application caused late winter hardening, frost injury and subsequent weakening of the trees leading to fungal infection.

Mycorrhizae: Mycorrhizae are symbiotic associations between plant roots and fungi. Mycorrhizal associations are found virtually in every higher plant family (Harley, 1969). Those associations result in a number of benefits to the host plant: (1) Increase in the longevity of the fine roots; (2) Increase in the rate of nutrient absorption from the soil; (3) Selective absorption of certain ions from the soil; (4) Improved nutrient cycling; (5) Resistance to certain root pathogens; (6) Increase in tolerance to soil toxins, cold and high temperatures; and (7) Tolerance to adverse soil pH and excess cations and anions (Hayman, 1978; Marx and Krupa, 1978). With the exception of the nutrient relationships and to a degree resistance to pathogens, mechanisms governing the other benefits are not well understood.

Symbiotic fungal infection of plant roots and successful mycorrhizal development depends on the supply of carbohydrates from the host to the fungus. In return, the fungus supplies the host with otherwise limiting nutrients, including N. There is evidence that plants adapted to N limiting soils (e.g., conifers, members of the cucumber family) have evolved with an N conservation mechanism, ornithine or urea cycle in their root system. While most amino acids contain one atom of N, intermediates in the ornithine cycle such as citrulline and arginine contain 2 and 3 N atoms per molecule. In the absence of mycorrhizal association, this cycle becomes non-operational due to mineral deficiency and more importantly, because the by-product of the conversion of arginine to ornithine, urea, is toxic to higher plants. Mycorrhizal infection resulting in sufficient supply of minerals to the host roots removes the blockage of the ornithine cycle leading to the availability of additional N and efficient amino acid metabolism and protein biosynthesis in the root. Equally importantly, most microorganisms including mycorrhizal fungi have the enzyme urease that detoxifies the urea released during the conversion of arginine to ornithine, the latter leading to the formation of glutamate, a key amino acid (Krupa et al., 1973; Krupa and Bränström, 1974).

NH_y assimilation requires carbon skeletons and may thus compete with mycorrhizal sinks and inhibit mycorrhizal development and growth. Since mycorrhizae are of great importance for ion uptake, nutrient imbalances caused by NH_y uptake may further be increased (Bledsoe and Rygiewicz, 1986). It is well known that fertilization of forest stands can reduce mycorrhizal development (Menge and Grand, 1978). Therefore, it has been suggested that atmospheric nitrogen deposition has similar effects as fertilizer application (Nihlgård, 1985).

4.2.3 Interactive Effects of NH_y with Other Air Pollutants on Vegetation

Very few experiments have been conducted to study the combined effects of NH_3 with other air pollutants such as SO_2 or ozone (O_3). Since one of the effects of O_3 is to accelerate leaf senescence (Pell et al., 1997), and conversely since NH_y is known to prolong the growth period and retard senescence, one might expect O_3 and NH_y to negate the effects of each other. However, the modes of action of these two pollutants are completely different. The toxic effect of O_3 *per se* is dependent on the amount of uptake and detoxification by the antioxidant defense system of the plants (Pell et al. 1997). Since the antioxidant systems require energy to operate, even successful detoxification of O_3 may increase the plant sensitivity to NH_y by decreasing the amount of energy available for NH_y assimilation. Another aspect to be considered is that NH_3 exposure tends to cause stomatal opening (Fangmeier et al. 1994; Krupa, 2002). Thus the amount of O_3 uptake may be increased in the presence of NH_3.

4.2.4 Effects of N Deposition at the Ecosystem Level

Anthropogenic N input affects its status and cycling in ecosystems both through the soil and plant canopy deposition, leading to eutrophication of coastal marine waters (Burkart and James, 1999), and to acidification of the soils (Fenn et al. 1998, also see Krupa, 2002). Since natural terrestrial ecosystems are usually N deficient (most of the N pool originates from N_2-fixation rather than from weathering and is present as organic N), excess N from deposition is readily taken up and accumulated until saturation occurs. According to Tamm (1991), ecosystems in the saturation phase are characterized by an amount of N supply meeting all their requirements, with simultaneous leaching of NO_3^-. It is clear that N deposition has steadily increased during the past 100 years, so that most ecosystems are assumed to be in the accumulation or already in the saturation phase (Fenn et al. 1998; also see Krupa, 2002).

Ecological modification and successional change by means of N deposition will be most obvious in systems poor in N, because species adapted to N deficiency will soon be out-competed by species with higher N demand (Aerts, 1990; Tilman and Wedin, 1991). Therefore, species diversity may be severely reduced by nitrogen eutrophication (Ellenberg, 1985). Besides eutrophication, acidification may cause floristic alterations. Overall, nitrogen deposition may have severe consequences for species diversity and nature conservation (Woodin and Farmer, 1993).

4.2.4.1 Soil Processes

Nitrogen saturation and acidification of the soil are symptoms of changes in a complex network of interacting processes that are influenced by atmospheric input and indirectly by effects on vegetation and soil microflora and microfauna. The population of soil microfauna generally declines due to acidification and as a consequence decomposition and mineralization of organic matter slows down (Van Straalen et al., 1988). Decomposition and mineralization of organic material is also influenced by N deposition via its impact on biomass production and the chemical composition of the vegetation (Berendse, 1990).

N saturation: Unfertilized terrestrial ecosystems are usually characterized by relatively closed N cycling, i.e., N input and output are comparably small in relation to N exchange within the soil/plant subsystem. In these ecosystems, N is usually limiting for productivity and additional nitrogen is readily absorbed and utilized. If deposition exceeds the capacity to utilize N for a considerable period of time, over-saturation of the system (Tamm, 1991) indicated by N loss (Nilsson et al., 1988; Tamm, 1989; Rosen et al., 1992) will occur. N loss may occur either by leaching of NO_3^- which is more mobile than NH_4^+ (Grennfelt and Hultberg, 1986) or by denitrification, yielding N_2 and some N_2O.

Acidification: NH_4^+ deposited to the soil may either be taken up by plant roots or be subjected to nitrification yielding NO_3^-. Since both processes result in proton release into the soil, acidification will occur, particularly in acid soils with low buffering capacity. Subsequently leaching of cations such as K^+, Ca^{2+} and Mg^{2+} leading to nutrient imbalances for plant growth and release of toxic ions such as Al^{3+} may occur (Van Breemen et al., 1984; Reuss et al., 1987; Nilsson et al., 1988; Van Dijk et al., 1989; Tomlinson, 1991).

4.2.4.2 Ecosystem Responses

Effects on heathlands: The most obvious vegetation change in Dutch heathlands during the past few decades has been their transition into grassland (Heil and Diemont, 1983), both in dry (dominated by *Calluna vulgaris*) and wet heathlands (dominated by *Erica tetralix*, cross-leaved heath). Similar vegetation changes were observed in northern Germany (Steubing and Buchwald, 1989).

Effects on species-rich grasslands: N deposition severely reduces species diversity in calcareous grasslands of Central Europe by promoting the dominance of *Brachypodium pinnatum* (false-brome). The grass species benefited from N input more than other chalkland species, without suffering from lowered P availability caused by N-induced growth stimulation (Bobbink, 1991).

Effects on forests: Until the 1980-1990s, the 'classical' forest decline theories such as due to SO_2 pollution or acidic rain were most popular. However, at the present time, it is well accepted that forest decline is a result of complex interactions of both of natural and anthropogenic stresses. These include climatic events, e.g., early or late frost, drought periods and biotic stress such as pathogens and pests, management practices, air pollution, and possibly global climate change (McLaughlin, 1985; Krause et al., 1986; Klein and Perkins, 1988; Innes and Oleksyn, 2000).

Nihlgård (1985) was the first to consider N deposition from NH_y and NO_x as significant contributors to forest decline in Europe. Taking into account all the direct and indirect effects of N deposition previously described and considering the receptor qualities of forest canopies to atmospheric deposition, N deposition must indeed be regarded as a factor severely disturbing nutrient cycling in forest ecosystems with detrimental effects for tree health (Fenn et al. 1998, also see Krupa, 2002).

Effects on epiphytic lichens and green algae: Lichens (seedless, flowerless lower plants, products of symbiosis between algae and fungi) and green algae are integral parts of the forest ecosystems. Different epiphytic lichen assemblages are found on tree barks that are acidic or nutrient-poor ("acidophytic") (e.g., oak and beech) and neutral or nutrient-rich or "eutrophicated" ("nitrophytic") (e.g., willow, elm and poplar) (van Dobben and Ter Braak, 1998).

Van Dobben and ten Braak (1999) studied the relationships between measured concentrations of SO_2, NO_2 and NH_3 and lichen abundance in the Netherlands. They compared the observed relationships to published indicator scales of lichen sensitivity to air pollution. For SO_2, a good agreement was found between all the indicator scales and calculated sensitivities based on the presence or absence of a given species. For NO_2 and NH_3 the correspondence was less obvious. The sensitivity to NH_3 was inversely related to the Wirth's (1991) acidity indicator scale. Species that react positively to NH_3, tended to be sensitive to SO_2 and NO_2.

Although at the outset, increases in the abundance of "nitrophytic" lichens may appear to be correlated with increases in N deposition, such lichen species appear to have become more common with decreases in SO_2 concentrations and/or S deposition (acidification) (Poikolainen et al., 1998a; van Dobben and Ter Braak, 1998).

It has been observed that increased N deposition resulted in changes in vegetation, especially in areas of high deposition in Central Europe, to the extent eutrophic plant species have increased at the expense of oligotrophic species (Bobbink et al., 1992c; Sutton et al., 1993). At the same time, epiphytic algae have increased especially on Norway spruce (*Picea abies*) needles in the southern parts of Fenno-scandia and in Central Europe (Göransson, 1988, 1990; Bråkenhielm and Liu Qinghong, 1995).

According to Poikolainen et al. (1998b) the abundance of green algae may have been caused by several concurrent changes in the environment. A slight increase in mean annual temperature, a long-term stability in N deposition and a clear decrease in S deposition may all have contributed to the increased growth and abundance of green algae. Multi-variate, source apportionment studies are required to better explain the relationships between N deposition and the distributions of epiphytic green algae, as well as the lichens.

4.2.5 Air Quality Indicators for Protecting Vegetation

The critical level/critical load concept has been followed in many countries over the last two decades and has been widely accepted as an appropriate tool to provide estimates of target levels/target loads for decision makers (Bull, 1991).

Critical levels are defined as 'the concentrations of pollutants in the atmosphere above which direct adverse effects on receptors, such as plants, ecosystems or materials may occur according to present knowledge' (UNECE, 1988).

Critical loads concept was originally developed in Canada in the 1970s. Critical loads are defined as 'A quantitative estimate of an exposure to one or more pollutants below which harmful effects on specified sensitive elements of the environment do not occur according to present knowledge' (Nilsson and Grennfelt, 1988).

There is inevitably some debate on how to define 'adverse or harmful effects'. In particular, this is true for NH_3 that acts as a fertilizer at low concentrations without any detectable (primary) toxic effects. However, secondary effects such as increased susceptibility to stress or altered competitive ability (mostly not investigated or not detected in short term experiments) may occur. Nevertheless, the United Nations Economic Commission for Europe (UNECE, 1994), adopted the critical loads approach.

4.2.5.1 Critical Levels (NH_3)

Table 14 provides a listing of critical levels for NH_3 given by different investigators. The values obtained by Van der Eerden (1982) and Posthumus in UNECE (1988) in Table 14 were estimated using an approach that may not be appropriate according to Fangmeier et al. (1994). Van der Eerden et al. (1991) used a toxicological model described for water pollution by Kooijman (1987) and for soil pollution by Van Straalen and Denneman (1989) to recalculate critical levels for NH_3. Those values are shown in Table 14 and are far below the previous estimates.

Table 14 Critical Levels for Exposure of Vegetation to NH_3

NH_3-concentration ($\mu g/m^3$)^a	Duration	Reference
300	1 year	Van Haut et al. (1979)
10,000	1 hour	Van der Eerden (1982)
600	1 day	
75	1 year	
10,000	1 hour	Posthumus in UNECE (1988)
600	1 day	
100	1 year	
3,300	1 hour	Van der Eerden et al. (1991)
270	1 day	
23	1 month	
8	1 year	
276	1 day	Van Der Eerden et al. (1998)
20-50	1 month	

To convert µg m-3 to ppb, multiply by 1.44 (at 25°C and 1 atmosphere)

Source: modified from Fangmeier et al (1994)

Fangmeier et al. (1994) tried to apply an ecotoxicological model to estimate critical levels for four different groups of plants: (a) natural vegetation as a whole, (b) most sensitive species such as members of the *Viola canina* group and mosses, (c) trees and (d) agricultural crops (Hadwiger-Fangmeier et al., 1992). However, the amount of available data (observations) was too small in many cases, to calculate critical levels for NH_3 for corresponding plant groups. Nevertheless, the range of susceptibility to NH_3 was suggested to be: natural vegetation > forests > crops, assuming forests to include managed systems and natural vegetation to include native woodlands.

4.2.5.2 Critical Loads (N)

Examples of estimates and model calculations of critical loads of N are presented in Table 15. In many cases (particularly in Europe), current N deposition by far exceeds those critical load values. In a 1996 report by the Danish Environmental Protection Agency (full English translation not available, http://www2.mst.dk/magazile/issue1/ammonia2/fakta1.htm), critical loads stipulated for ammonia and other N species was 5 and 10 kg ha^{-1} $yr^{-1}$for heaths and bogs respectively. For forests, 10-20 kg ha^{-1} yr^{-1}, depending on the soil conditions. According to the report, if N deposition were evenly distributed across entire Denmark, it would equal an average of 21 kg ha^{-1} yr^{-1}, with 14 kg attributable to NH_3 and the remaining 7 kg to NO_x (primarily fossil fuel combustion).

Natural and semi-natural ecosystems, as well as forests must be expected to be severely at risk from the current amount of N deposition. Agricultural crops appear to be the only systems not negatively influenced at present, since high productivity and turnover prevent the accumulation of N. In the overall analysis, one should keep in mind, however, that N_2O release to the atmosphere and NO_3^- leaching into the ground water by agricultural systems represent potential problems, which may be increased by N deposition into these systems.

4.2.6 Discussion

At the global scale, among all N species in the atmosphere and their deposition on to terrestrial vegetation and other receptors, NH_3 is considered to be the foremost. The major sources for atmospheric NH_3 are agricultural activities and animal feedlot operations, followed by biomass burning (including forest fires) and to a lesser extent fossil fuel combustion. Close to its sources, acute exposures to NH_3 can result in visible foliar injury on vegetation. NH_3 is deposited rapidly within the first 4-5 km from its sources. However, NH_3 is also converted in the atmosphere to fine particle NH_4^+ aerosols that are a regional scale problem.

Much of the current knowledge of the effects of NH_3 on plants is predominantly derived from the studies conducted in Netherlands. Adverse effects on vegetation occur when the rate of foliar uptake of NH_3 is greater than the rate and capacity for in vivo detoxification by the plants. Most to least sensitive plant species to NH_3 are native vegetation > forests > agricultural crops.

Table 15 Critical Loads for N

Ecosystem	Critical load (kg N ha^{-1} yr^{-1})	Reference
Forests on silicate soil	3-14	Schulze et al. (1989)
Forests on calcareous soil	3-48	Schulze et al. (1989)
Acidic (managed) coniferous forest	15-20	Anon. (1992), Bobbink et al. (1992b)
Acidic (managed) deciduous forest	<15-20	Anon. (1992), Bobbink et al. (1992b)
Lowland dry-heathland	15-20	Anon. (1992), Bobbink et al. (1992b)
Lowland wet-heathland	17-22	Anon. (1992), Bobbink et al. (1992b)
Species-rich heaths/acidic grasslands	<20	Anon. (1992), Bobbink et al. (1992b)
Arctic and alpine heaths	5-15	Anon. (1992), Bobbink et al. (1992b)
Calcareous species-rich grassland	14-25	Anon. (1992), Bobbink et al. (1992b)
Neutral-acid- species-rich grassland	10-15	Anon. (1992), Bobbink et al. (1992b)
Montane-subalpine grassland	10-15	Anon. (1992), Bobbink et al. (1992b)
Mesotrophic fens	20-35	Anon. (1992), Bobbink et al. (1992b)
Ombotrophic bogs	5-10	Anon. (1992), Bobbink et al. (1992b)
Heather, bogs	5-10	Danish EPA[a]
Forests	10-20	Danish EPA[a]

[a] See section on 'Critical loads' for details

Source: modified from Fangmeier et al (1994)

In addition to the direct foliar injury, adverse effects of NH_3 on plants include alterations in: growth and productivity, tissue content of nutrients and toxic elements, drought and frost tolerance, responses to insect pests and disease causing microorganisms (pathogens), development of beneficial root symbiotic or mycorrhizal associations and inter species competition or bio-diversity. In all these cases, the joint effects of NH_3 with other air pollutants such as the all-pervasive O_3 or the increasing SO_2 concentrations are poorly understood.

While NH_3 uptake in plants occurs through the shoots, NH_4^+ uptake occurs through the shoots, roots and through both pathways. However, NH_4^+ is immobile in the soil and is converted to NO_3^-. In agricultural systems, additions of NO_3^- to the soil (initially as NH_3 or NH_4^+) and the consequent increases in the emissions of N_2O (a greenhouse gas) and leaching of NO_3^- into the ground and surface waters are of major environmental concern.

At the ecosystem level NH_3 deposition cannot be viewed alone, but in the context of total N deposition. There are a number of forest ecosystems in North America (including Canada) that have been subjected to N saturation and the consequent negative effects. Regulatory mitigative approaches to these problems include the use of N saturation data or the concept of critical loads. Current information suggests that a critical load of 5 to 10 kg ha^{-1} yr^{-1}of total N deposition (both dry and wet deposition combined of all atmospheric N species) would protect the most vulnerable terrestrial ecosystems (heaths, bogs, cryptogams) and values of 10 to 20 kg ha^{-1} yr^{-1} would protect forests, depending on their soil conditions. However, to derive the best analysis, the critical load concept should be coupled to the results and consequences of N saturation.

The following points are concluded based upon this review:

- NH_3 is taken up into the leaves by diffusion through the stomata. Acute exposures to NH_3 (e.g., 0.03 mg/m^3 or 43 ppb for 23 days or < 0.5 mg/m^3 or 0.72 ppm for 7 days) can result in visible foliar injury on plants. Acute NH_3 injury symptoms on broad-leafed plants (death of tissue between the veins) can be confused with similar symptoms caused by acute exposures to SO_2.
- At low concentrations, NH_3 can stimulate plant growth. However, regarding negative effects on biomass, heath and bog vegetation and cryptogams (flowerless, seedless plants) are considered to be most sensitive to NH_3 exposures (e.g., 0.05 $\mu g/m^3$ or 72 ppb for 90 days).
- NH_3 assimilation by plants can result in significant increases in tissue organic nitrogen and alterations in nutrient content and accumulation of undesirable elements such as Al^{3+}.
- In assessing the effects under ambient conditions, NH_3 should not be evaluated singly, but together with NH_4^+ (combined NH_y). While NH_3 is taken up through the shoots, NH_4^+ is taken up both through the shoots and roots. Appropriate levels of NH_y cannot only alter growth and biomass, but also increase sensitivity to drought and reduce frost hardiness.
- The joint effects of NH_3 on plants, in the presence of other air pollutants such as SO_2, NO_2 and O_3 are very poorly understood. Such joint effects can be additive, more than additive or less than additive.
- Of much concern is the suppression of mycorrhizae (beneficial or symbiotic associations between plant roots and certain soil fungi) by excess NH_y and NO_3^-. Absence of mycorrhizae will lead to significant nutrient deficiencies and decline in plant growth and productivity.
- There is clear evidence from central Europe (particularly The Netherlands) that excess NH_y and N deposition has resulted in alterations in the structure and diversity of native plant communities such as the heather bogs.
- There are a number of forest ecosystems in North America, including Canada, which have already undergone N saturation. Information on levels of deposition resulting in N saturation coupled with the critical load concept would be a desirable approach in mitigating the adverse effects of excess N. However, such a strategy should consider the geographic distributions of ecosystem types.

In a decreasing order of sensitivity to excess N are: native vegetation > forests > agricultural crops. Although negative effects of excess N on crops are highly unlikely, excess N can result in increased emissions of N_2O (a greenhouse gas) and increased leaching of N and run off into ground and surface waters (as in the Mississippi River basin) resulting in eutrophication of coastal marine zones and other undesirable effects. Phosphate is regarded as a more common cause of eutrophication.

4.3 Materials

The effect on materials from exposure to an individual air pollutant is difficult to separate from the effect of others. Many of the effects on materials have been ascribed more to the multi-pollutant situation that exists in urban environments than to the action of separate pollutants. Ammonia may contribute to material damage in several ways, but its role is not yet clarified. The role of ammonia may be similar compared to that of:

- rain, carbon dioxide and sulphur dioxide for calcareous stonework,
- oxygen, sulphur dioxide and wetting by rain, condensation, mist, etc. on metals,
- ozone for dyes, fabrics, plastics and elastomers

The discussion presented here is limited to the effects the multi-pollutant situation that exists in urban environments or to that of acidic deposition because of a lack of data exists on damage mechanisms for ammonia alone.

The effects of air pollutants on materials (e.g. buildings, fabrics, etc.) include discoloration, failure of protective coatings, loss of detail in carvings and structural failure (US-Canada, 2000; Lipfert, 1989). In the public arena most concern about pollutant damage to materials has focused on historic monuments. However, impacts of air pollution have also been recorded on modern buildings and to other types of materials such as textiles, leather and paper. Given the relative abundance of modern buildings compared to older ones, it may be anticipated that damages to the former will outweigh those to the latter.

4.3.1 Stone

The primary concern in regard to air pollution is the soiling and deterioration of limestone (Haynie et al., 1976). Limestone is widely used as a building material and for marble statuary. Many buildings in older cites have been exposed to urban smoke, SO_2 and other acid-forming gases, and CO_2 for decades. The evolution of soiling patterns on limestone buildings is hypothesized to result from two competing processes: (1) the deposition of air pollutants to the stone and (2) the dissolution and washing of stone surfaces by rain. The surfaces have become soiled and are subjected to chemical attack by acid gases. SO_2 and moisture react with limestone ($CaCO_3$) to form calcium sulphate ($CaSO_4$) and gypsum. These two sulphates are fairly soluble in water, causing deterioration in blocks and in the mortar used to hold the blocks together. CO_2 in the presence of moisture forms carbonic acid ($H_2CO_{3,aq}$). This acid converts the limestone to bicarbonate, which is also water-soluble and can be leached away by rain. This type of mechanism is present in the deterioration of marble statues.

Other possible mechanisms of deterioration of limestone reported to exist are poorly understood (US-Canada, 2000). Another hypothesis is looking at the role of microorganisms in limestone degradation in the presence of air pollutants. Sulphur-utilizing and hydrocarbon-degrading microorganisms are reported to be present at higher levels in limestone in polluted areas compared to stones in clean environments.

4.3.2 Brickwork, Mortar and Rendering

Observation in major cities suggests that brick is unaffected by sulphur dioxide attack. However, although brick itself is relatively inert to acid damage, the mortar component of brickwork is not.

The primary mechanism of mortar erosion is acid attack on the calcareous cement binder (Lipfert, 1989).

4.3.3 Concrete

The major binding agent in most concrete is an alkaline cement which is susceptible to acid attack. Potential impacts to concrete include soiling/discoloration, surface erosion, spalling and enhanced corrosion of embedded steel. However, for all these impacts (with the exception of surface erosion) damages are more likely to occur as a result of natural carbonation and ingress of chloride ions, rather than interaction with pollutants such as SO_2. Effects on steel embedded in reinforced concrete are possible, but no quantitative information exists for these processes. In view of this damage to concrete has not been considered in the study.

5.0 RISK CHARACTERIZATION

Risk characterization of an ambient air contaminant involves the integration and evaluation of several types of key information. Where it is undertaken for a site-specific situation, such as for the screening assessment of proposed industrial emissions of NH_3, quantitative approaches can be used. For example, US EPA (1989) provides guidance for human health risk assessments and US EPA (1998, 1997, and 1992) offer guidance for ecological risk assessments for a site-specific situation. For ambient air exposures, this may involve taking measurements or using a computer dispersion model to estimate ambient ground-level concentrations of NH_3 under different averaging times and making comparisons to safe levels of exposure.

For the general case, however, use of site-specific risk characterization approaches is limited unless a number of assumptions are made. The emission characteristics for sources of NH_3 release to air in Alberta vary for non-point sources, such as intensive livestock operations and biomass burning (forest fires), and for point sources, such as industrial emissions. This variability is difficult to represent as a general case for quantitative assessment and the resulting risk characterization would have substantial uncertainty. As a result, a qualitative risk characterization approach is used to evaluate issues associated with NH_3 in ambient air. The types of key information evaluated can include, but not be limited to:

- relevant chemical species in air,
- pathways by which exposure may occur,
- human and ecological receptors, and material that may be exposed,
- relevant potential effects endpoints (impacts)

These issues are discussed further below.

5.1 Relevant Chemical Forms

Ammonia released into the environment, as discussed previously, can remain in its original gaseous state or participate in a number of rapid gas phase, liquid phase, thermal or photochemical reactions. Reactions with sulphur dioxide (SO_2) or ozone (O_3) produce aerosols that eventually return to the surface as wet or dry deposition.

The majority of NH_3 emitted to the atmosphere is converted to the ammonium particulate/ammonium (NH_4^+) aerosol, while the balance is in the gaseous state. Thus, gaseous NH_3 and the NH_4^+ aerosols represent relevant ammonia species of interest. While both forms may be present in the atmosphere close to sources, the aerosols have slightly longer atmospheric residence times (i.e. days) compared to gaseous ammonia (hours).

5.2 Exposure Assessment

5.2.1 Humans

In considering the potential for inhalation exposure for humans, background levels of ammonia gas in community ambient air tend to be low. Greater variability in ambient levels of ammonia gas are expected near non-point and point sources.

5.2.2 Vegetation

Close to sources, vegetation exposures to NH_3 and NH_4^+ (NH_y) can be expected to occur. NH_y is deposited rapidly within the first 4 to 5 km from sources. While vegetation exposures to NH_y can be expected at greater distances from sources, they are of considerable less importance than that occurring closer to the sources.

5.2.3 Materials

The implication of material effects from exposure to ammonia is difficult to separate from the effect of other air pollutants. However in urban environments with important industrial point sources of ammonia, the role of multi-pollutant – including ammonia – exposures may be an issue where material damage is occurring.

5.3 Toxicity Assessment

5.3.1 Human Health

5.3.1.1 Potential Health Effects of Exposure

Two different types of potential health effects are relevant for ammonia: acute non-cancer effects that result from short-term exposure; and chronic non-cancer effects that result from long-term (chronic) exposures. The specific conditions of ammonia exposure to animals and/or man corresponding to these types of effects vary and were further discussed in Section 4.

In general, acute health effects reported in animals following short-term inhalation of ammonia may include oral, nasal and eye irritation; respiratory tract irritation; decreased respiratory rate; increased respiratory depth; reduced body weight; and lethargy. The acute effects of ammonia inhalation by humans are similar to those reported in animal studies and include oral, nasal and eye irritation; respiratory tract irritation; and increased respiratory depth.

The health effects following chronic exposure of animals to ammonia via inhalation may include nasal irritation; inflammatory response in lungs; reduced olfactory acuity; and lethargy. Animal studies have also demonstrated that ammonia exposure reduces immune response and increases susceptibility to bacterial infection of the respiratory tract. Chronic effects reported in humans include reduction in pulmonary function; cough; phlegm; wheeze; and dyspnea.

5.3.1.2 Dose-Response Measures for Risk Assessment

Dose-response measures or safe levels of exposure used for risk assessment have been derived by California Environmental Protection Agency (Cal EPA), US Agency for Toxic Substances and Disease Registry (ATSDR), and US Environmental Protection Agency (US EPA).

Acute: Cal EPA derived a safe level of exposure to protect against eye and respiratory irritation under short-term (acute) exposure situations. An acute reference exposure level (REL) of 3,200 $\mu g/m^3$ (4,600 ppb) for a 1-hour averaging time was derived using human exposure-response data pooled from four previous studies and a "toxic load" (concentration x time) approach (Cal EPA, 1999). The acute REL was calculated by identifying a benchmark concentration (BC) using a log-normal probit analysis of data pooled from the four studies and applying an uncertainty factor (UF) of 3 to account for intraspecies variation in the human population (Cal EPA, 2000).

Chronic: ATSDR derived a safe level of exposure to protect against respiratory irritation under long-term (chronic) exposure situations (referred to as a minimum risk level or MRL of 208 $\mu g/m^3$ – 300 ppb) (ATSDR, 1990). A no-observed-adverse-effects-level (NOAEL) from a single human occupational 15-week study of chronic-duration inhalation exposure was used to derive the MRL. After adjusting for intermittent exposure, the NOAEL was divided by a safety factor of 10 for human variability.

US EPA derived a safe level of exposure to protect against decreased pulmonary function and changes in subjective syptomatology under long-term (chronic) exposure situations (reference concentration, RfC, of 100 $\mu g/m^3$ or 144 ppb) (US EPA, 2001). A human equivalent concentration (HEC) lowest-observed-adverse-effects-level (LOAEL) of 2,300 $\mu g/m^3$ was adjusted with a total uncertainty factor of 30, and after rounding to one significant digit, a value of 100 $\mu g/m^3$ was derived.

5.3.2 Vegetation

Potentially, there are a large number of ecological receptors and impact pathways within an ecosystem that may affect the ecosystem's function. However, based upon a review of vegetation impacts (Krupa, 2002), it is realistic to acknowledge that scientific information is reported for only a fraction of these receptors and impact pathways.

Assuming that forests include managed systems and natural vegetation includes native woodlands, the range of susceptibility to adverse responses from vegetation exposure to NH_3 is suggested to be natural vegetation > forests > crops. In addition, critical exposure concentrations cover a wide range depending upon the exposure duration (Table 16). Table 16 summarizes data previously presented in Table 14. It is worth noting that concentration-response measures for the protection of acute and chronic health effects in humans are on the same order as concentrations shown in Table 16, indicating that human health-based criteria for ammonia may be adequate for protection of vegetation.

Table 16 **Range of Estimated Critical Concentrations for Vegetation Exposure to NH_3 (summarized from Table 14)**

NH_3 concentration ($\mu g/m^3$)	Duration
3,300 to 10,000	1 hour
270 to 600	1 day
20 to 50	1 month
8 to 300	1 year

Other criteria have been proposed for protecting vegetation and ecosystems and are in the form of critical nitrogen-N deposition loading (Table 15). Krupa (2002) reported that N deposition in other areas (i.e. outside of Alberta) has been shown to exceed these critical load values proposed in Table 15. Natural and semi-natural ecosystems, as well as forests might be expected to be at risk from the amount of N deposition in these areas. Agricultural crops appear to be the only systems not negatively influenced at present, since high productivity and turnover prevent the accumulation of N.

5.4 Characterization of Risk

The range of exposure concentration guidelines proposed by various agencies for protection of human and vegetation are shown in Figure 4 for different averaging time periods. The exposure concentration guidelines for protection of human receptors are summarized from data presented in Table 18, while exposure concentration guidelines for protection of vegetation were obtained from data presented in Table 16. Also show in Figure 4 is the range of hourly maximum ammonia concentrations reported on a monthly basis at several monitoring locations in Alberta based on data presented earlier in Table 9.

Figure 4 indicates that exposure concentration guidelines for protection against acute (short term) and chronic (long term) health effects in humans are on the same order as concentrations for vegetation. In addition, Figure 4 illustrates that the range of observed hourly maximum ammonia concentrations at selected monitoring locations in Alberta (in proximity of numerous industrial point sources and in the community of Fort Saskatchewan) overlaps with the range of hourly exposure concentration guidelines for human and vegetation receptors. These observations clearly support the need to have an ammonia guideline in place for air quality management purposes.

The effect on materials from exposure to an individual air pollutant is difficult to separate from the effect of others. Many of the effects on materials have been ascribed more to the multi-pollutant situation that exists in urban environments than to the action of separate pollutants. Ammonia may contribute to material damage or deterioration in several ways, but its role and corresponding exposure concentrations and duration are not yet clarified in the literature.

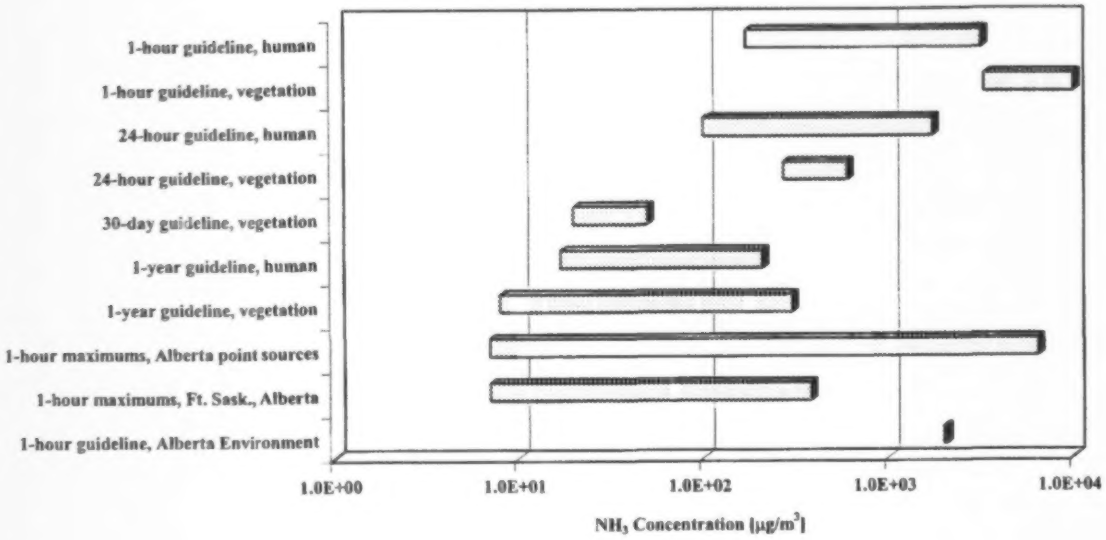


Figure 4 Range of Exposure Concentration Guidelines for Ammonia Proposed by Various Agencies for Protection of Human and Ecological Receptors

6.0 AIR SAMPLING AND ANALYTICAL METHODS

6.1 Reference Methods

In general, standard air monitoring methods and technologies for ammonia involve pump-and-tube sampling approaches using short-term detector tubes with a variety of subsequent analytical approaches. These techniques are more suited for personal, occupational and area monitoring than for ambient monitoring. Therefore, other methods should be used to determine long-term ambient ammonia concentrations since short-term detector tubes offer only spot checks of the local environment.

Widely employed and accepted referenced air monitoring methods and technologies for ammonia have been developed, tested and reported by the National Institute of Occupational Safety and Health (NIOSH) and Occupational Safety and Health Administration (OSHA). These methods are indicated below and described more thoroughly in Appendix B. Refer to Table 17 for individual method advantages and disadvantages. Additional methods are currently used in practice by many jurisdictions but are not considered standard methods and are discussed in Section 6.2.

NIOSH currently has two methodologies for the determination of ammonia in air – NIOSH Method 6015 and 6016. In both cases, sampling is conducted by drawing a known volume of air through a solid sorbent tube using a personal sampling pump. The working concentration ranges for these methods are 0.14 to 280 mg/m^3 for a 10-L sample and 17 to 68 mg/m^3 for a 30-L sample, respectively.

The current methodology used by the OSHA to determine ammonia in air (OSHA Method 188) consists of using a personal sampling pump to draw a known volume of air through a glass tube containing carbon beads impregnated with sulfuric acid (OSHA, 1991; Bishop et al., 1986). The reliable quantitative detection limit of the overall procedure is 1 mg/m^3 for a 24-L sample and 3.3 mg/m^3 for a 7.5-L sample. These high levels render this method unsuitable for ambient monitoring situations.

6.2 Alternative, Emerging Technologies

A variety of analyzers and measuring methods for assessing concentrations of ammonia in ambient air even at very low levels have been reported in a number of reviews (Appel et al., 1988; Manninen, 1988; Sickles et al., 1990; Wiebe et al., 1990; Williams et al., 1992; Mennen et al., 1996). Generally, these monitoring methods can be divided into two categories: those that allow time-integrated measurements (i.e. time-weighted averages) and those that allow continuous measurements.

The time-integrated monitoring methods and technologies include: filter packs and non-automatic annular denuder systems (Ferm, 1979; Allegrini et al., 1987; Ferm et al, 1988; Koutrakis et al., 1989; Harrison and Kitto, 1990; Andersen and Hovmand, 1994; Mennen et al., 1996; Sioutas et al., 1996); and passive samplers (Rudling et al., 1984; Schjoerring et al., 1992; Kasper and Puxbaum, 1994; Frenzel et al., 1995; Thijsse et al., 1998; Kirchner et al., 1999; Rabaud et al., 2001).

Continuous monitoring methods and technologies include: continuous-flow automated annular denuders (Wyers et al., 1993; Mennen et al., 1996; Erisman et al., 2001); scrubber and sniffer methods (Abbas and Tanner, 1981; Pranitis and Meyerhoff, 1987; Frenzel, 1994; Sorensen et al., 1994); chemiluminescence NO_x monitors with an NH_3 converter (Breitenbach and Scelef, 1973; Mennen et al., 1996; Alberta Environment, 2001); automated thermodenuders (Braman et al., 1982; Keuken et al., 1989; Langford et al., 1989; Romer et al., 1994); and advanced optical methods like DOAS (Gall et al., 1991), TDLAS (Cappellani et al., 1985; Mennen et al., 1996), FTIR (Tuazon et al., 1978), PTD (De Vries et al., 1995; Owens et al., 1999), and PF/LIF (Schendel et al., 1990). Most of these instruments have been studied and validated in field experiments (Ferm et al., 1988; Appel et al., 1988; Harrison and Kitto, 1990; Sickles et al., 1990; Wiebe et al., 1990; Allegrini et al., 1991; Williams et al., 1992; Adema et al., 1993; Mennen et al., 1996; Sioutas et al., 1996: Kirchner et al., 1999).

The reader is referred to Appendix B for a more complete description of these measurement technologies and corresponding detection limits and advantages/disadvantages.

Table 17 Method Advantages and Disadvantages

Method	Advantages	Disadvantages
NIOSH Method 6015	NA	NA
NIOSH Method 6016	NA	NA
OSHA Method 188	Adequate sensitivity Simple, rapid and easily automated Specific for ammonium ion Exposure to H_2SO_4 reduced Can use other analytical procedures	Positive interferences from ammonium salts, monoethanolamine, isopropanolamine and propanolamine
Filter packs	Samples at low concentrations Simple and portable Modest equipment costs	Both over and under-estimation of concentrations can easily occur Long sampling times required Labour intensive
Non-automatic annular denuder systems	Samples at very low concentrations Avoids problems with negative and positive chemical artifacts Low equipment needs and costs	Very labour intensive Requires many manipulations for a single measurement Fine time resolution not possible
Passive samplers	Inexpensive and easy to use Provide high spatial resolution Do not require power supply Assess long-term concentrations Well-suited for remote monitoring	Not often used for ambient monitoring Only reasonable time resolution available when low-level contaminants are observed
Continuous-flow automated annular denuder systems	Continuous measurements possible Less labour intensive Very good time resolution and detection limit Risk of contamination reduced Long-term measurements possible Inexpensive and reliable	NA
Scrubber and sniffer	Simple, selective and mobile Able to sample for long periods Suitable for field measurements	NA
Chemiluminescence NOx monitors with NH_3 converter	NA	Lacks sufficient accuracy Detection limit inadequate
Automated thermodenuders	Less labour intensive Short resolution times Capable of sampling unattended for long periods	May overestimate concentrations at very low levels Relatively expensive
Advanced optical methods (DOAS, TDLAS, FTIR, PTD, and PF/LIF)	Directly allow for sensitive, rapid and quantitative ammonia detection Fully automated and well-suited for continuous measurements Lowest detection limits available Good time resolutions High spectral resolutions	Very expensive and bulky Require highly trained operators Use corrosive chemicals Fixed monitoring methods Require large amounts of power Cannot be run unattended for long periods

*NA denotes not available

7.0 AMBIENT GUIDELINES

Ambient guidelines for ammonia in jurisdictions other than Alberta, i.e. in Canada, United States and elsewhere were examined. These guidelines are summarized in Table 18. For the most part, the toxicological basis for these guidelines is irritation of the respiratory system from exposures in humans. Additional information on how these guidelines were developed and how they are used in practice is provided in Appendix C. Full reference citations of the information sources examined and the complete name of each jurisdiction is also provided in Appendix C.

In general, all jurisdictions have common uses for their guidelines in practice. These uses may include, but not be limited to:

- reviewing permit applications for sources that emit air pollutants to the atmosphere,
- investigating accidental releases or community complaints about adverse air quality for the purpose of determining follow-up or enforcement activity,
- determining whether to implement temporary emission control actions under persistent adverse air quality conditions of a short-term nature

The two principal approaches used by all the agencies to develop their ammonia guidelines are:

- Using an occupational exposure level (OEL) and dividing it by safety or adjustment factors. The most common OEL used by US state agencies is the 8-hour threshold limit value (TLV) of 17,000 $\mu g/m^3$ (25 ppm) adopted by the American Conference of Governmental Industrial Hygienists (ACGIH). The safety or adjustment factors are intended to account for issues such as: differences between eight-hour exposures in the workplace and continuous 24-hour environmental exposures, increased susceptibility of some people in the general population versus the relatively healthy worker, and uncertainty in the margin of safety provided in an occupational exposure limit.
- Using non-carcinogenic risk assessment procedures. A no-observed-adverse-effect-level (NOAEL) – or lowest-observed-adverse-effect-level (LOAEL) from a suitable animal or human study is used. It is then divided by a series of adjustment factors. The adjustment factors are intended to account for issues such as: differences between animals and humans, sensitivity of high risk individuals, use of a LOAEL instead of a NOAEL, and for extrapolation from less-than-lifetime exposures to chronic exposure.

7.1 Canada

The provinces of Alberta, Manitoba, and Ontario are the only Canadian jurisdictions for which information was found. Alberta Environment currently has an Ambient Air Quality Guideline of 1,400 $\mu g/m^3$ (2,000 ppb) for ammonia as a 1-hour average based on odour perception (AENV, 2000). Manitoba Conservation has a maximum acceptable level concentration of 1,400 $\mu g/m^3$ (2,000 ppb) for ammonia as a 1-hour average (Man. Cons., 2002). The Ontario Ministry of the

Table 18 Summary of Air Quality Guidelines for Ammonia (refer to Appendix C for agency reference)

Agency	Guideline Title	Guideline Value [µg/m³] Averaging Time:				
		30-min	1-hour	8-hour	24-hour	annual
Alberta Environment	Ambient Air Quality Guideline (AAQG):		1,400			
Manitoba Conservation	Maximum acceptable level concentration:		1,400			
Ontario MOE	Ambient air quality criterion (AAQC):[1]				100	
	Maximum point of impingement (POI):	3,600				
ATSDR	Chronic inhalation minimum risk level (MRL):					208
US EPA	Reference Concentration (RfC):					100
California EPA	Acute reference exposure level (REL):		3,200			
	Chronic REL:					200
Louisiana DEQ	Ambient air standard (AAS):			640		
Michigan DEQ	Initial threshold screening level (ITSL):				100	
New Hampshire DES	24-hour ambient air limit (AAL):				100	
	Annual AAL:					100
New Jersey DEP	Risk assessment approach is used, hazard quotient (HQ):					100
North Carolina ENR	Acceptable ambient level (AAL):		2,700			
Ohio EPA	Maximum acceptable ground-level concentration (MAGLC):		170			
Oklahoma DEQ	Maximum acceptable ambient concentration (MAAC):[2]				1,742	
Texas Natural Resource Conservation Commission (TNRCC)	Short-term effects screening level (ESL):		170			
	Long-term ESL:					17
Vermont ANR	Hazardous ambient air standard (HAAS):			1,800		
Washington State DOE	Acceptable source impact level (ASIL):				100	
Wisconsin DNR	Ambient air concentration (AAC):				432	

[1] Recommended or proposed

[2] For anhydrous ammonia.

NOTE: 1 µg/m3 = 1.44 ppb at 25°C and 1 atmosphere

Environment (MOE) recently recommended an annual guideline of 100 μg/m^3 (144 ppb) based on the inhalation Reference Concentration (RfC) for chronic exposure from the US Environmental Protection Agency (Ontario MOE, 2001). Ontario MOE currently uses a maximum point of impingement (POI) of 3,600 μg/m^3 (5,170 ppb) based on a 30-minute averaging time (Ontario MOE, 2001).

7.2 United States

The US Agency for Toxic Substances and Disease Registry developed a chronic inhalation minimum risk level (MRL) (ATSDR, 1990). A NOAEL from a single human occupational 15-week study of chronic-duration inhalation exposure was used to derive the chronic inhalation MRL of 208 μg/m^3 (300 ppb). MRLs are intended to serve as a screening tool to help public health professionals decide where to look more closely. The US Environmental Protection Agency developed a chronic inhalation reference concentration (RfC) of 100 μg/m^3 (144 ppb) (US EPA, 2001). The RfC is intended for use by US EPA staff in risk assessments, decision-making and regulatory activities.

The California Environmental Protection Agency adopted an acute reference exposure level (REL) of 3,200 μg/m^3 (4,600 ppb) (Table 18) based on eye and respiratory irritation in exposed humans (Cal EPA, 1999). In addition, Cal EPA uses a chronic inhalation REL of 200 μg/m^3 (287 ppb) (Cal, EPA, 2000).

Six state agencies use the ACGIH 8-hour TLV (17,000 μg/m^3 or 25 ppm) in development of various ambient guidelines for ammonia (refer to Appendix C). Finally, the inhalation reference concentration (RfC) for chronic exposure from the US Environmental Protection Agency is used by another four state agencies to develop various ambient guidelines (refer to Appendix C).

7.3 European Union

No information about ammonia guidelines in European member countries was found.

7.4 Australia/ New Zealand

The New Zealand Ministry of Environment and Ministry of Health recently proposed guidelines for selected air toxics, however ammonia – and non-carcinogenic substances, in general – were not included (New Zealand, 2000).

8.0 DISCUSSION

When establishing an ambient air guideline in the form of a concentration limit with a corresponding duration (i.e. averaging time), a number of factors may be taken into account for an air pollutant:

- nature of adverse health effects and conditions of exposure (e.g. exposure concentrations and duration) associated with these effects,
- estimated or actual degree of exposure of receptors, and in particular receptor groups that may be sensitive to the air pollutant,
- available technologies and associated economics for routinely or periodically monitoring for the pollutant in air,
- availability and suitability of approaches for screening and estimating ambient ground-level concentrations in order to compare to the guidelines for permit applications or other situation

Guidelines in the form of an acute (short term) and chronic (long term) duration are discussed below.

8.1 Acute Exposure Conditions

Acute health effects reported in animals following short-term inhalation of ammonia include oral, nasal and eye irritation; respiratory tract irritation; decreased respiratory rate; increased respiratory depth; reduced body weight; and lethargy. These types of effects have been observed in controlled animal studies at concentrations ranging from 50,000 to 500,000 $\mu g/m^3$ (72 to 720 ppm) over exposure durations ranging from 6 hrs (continuously) to 40 hrs (intermittently over 5 days). Similar acute effects of ammonia inhalation are reported for humans (oral, nasal and eye irritation, and respiratory tract irritation) for comparable exposure concentrations and durations.

Alberta Environment's current ambient air quality guideline (AAQG) for ammonia, as discussed previously, is 1,400 $\mu g/m^3$ (2,000 ppb) as a 1-hour average and is based on odour perception (AENV, 2000b). Alberta Environment sets ambient guidelines for some substances based on odour perception. In the case of ammonia, the reported odour threshold level ranges from 500 to 35,000 $\mu g/m^3$ (720 to 50,000 ppb) with a median on the order of 3,500 $\mu g/m^3$ (5,000 ppb).

The major sources for atmospheric emissions of ammonia in Alberta would be agricultural activities (animal feedlot operations and other activities), followed by biomass burning (including forest fires) and to a lesser extent fossil fuel combustion (industrial sources) and accidental releases. Ammonia concentrations observed in the Counties of Lethbridge and Warner, Alberta (areas with intensive feedlot activities) (AENV, 2000b), indicate that animal feedlot operations produce measurable amounts of ammonia in the immediate vicinity (discussed in Section 5).

Animal feedlot operations do not appear to be able to produce ambient concentrations of a sufficient amount to be of concern with respect to acute (short-term) health effects (e.g. compared to Cal EPA's derived reference exposure level of 3,200 µg/m^3 (4,600 ppb). Ammonia monitoring in areas of Alberta with intensive feedlot activities indicated concentrations greater than 50% of Alberta's AAQG. The locations of where these concentrations were observed were targeted immediately around animal feedlot operations. Thus, the current AAQG (which is odour based) would be a reasonable benchmark to apply to ammonia emissions from animal feedlot operations. This also appears to be the case for other sources – e.g. industrial sources – where higher ambient ammonia concentrations have been reported (e.g. refer to Table 9). In the case of accidental releases, ambient ammonia concentrations may be extremely high for short periods of time near release areas.

The current AAQG appears to be adequate in protecting against the reported acute effects of inhalation when compared to other short-term air quality guidelines developed using non-carcinogenic risk assessment procedures. For example, Alberta Environment's 1-hour average (1,400 µg/m^3 or 2,000 ppb) is less than that adopted by Cal EPA (3,200 µg/m^3 or 4,600 ppb) and North Carolina ENR (2,700 µg/m^3 or 3,900 ppb).

Direct comparison of the current AAQG to guidelines developed using occupational exposure levels (OELs) is cautioned. There are limitations in the direct and indirect application of OELs for ambient air quality guidelines for a number of reasons:

- OELs are based on information gathered in the workplace, through experience from medical research and practice, from experimental human and animal studies, and from a combination of these sources. Often they are based upon averaged tolerated doses from actual repeated industrial exposures. In this respect, they would be considered very accurate at predicting human adverse health effects in industrial exposure situations.
- OELs are determined for a population of workers who are essentially healthy and who fall within a working age group of about 17 to 65 years. These individuals are supposedly in the prime of life, and potentially less susceptible to the effects of hazardous substances than other members of the public. Individuals vary in sensitivity or susceptibility to hazardous substances, with the elderly and infants in general being more susceptible than healthy workers.
- For most substances, during a normal work schedule (8 hours per day, 5 days per week), a worker receives 40 hours of exposure per week with daily breaks and extended weekend periods in which the body may rid itself of the accumulated substances before elevated levels are reached. For a person living continuously in an environment containing such substances, however, these recovery periods do not exist.

For these reasons, agencies using OELs have a policy of adjusting them downward with the use of safety or adjustment factors to derive guidelines for environmental settings. The OELs are considered surrogates for benchmark values for ambient exposures only because they tend to be based upon a large body of toxicological, epidemiological, and/or clinical evidence pertaining to human exposure (albeit in the workplace). Uncertainty exists in terms of whether too much (or too little) safety is inherent in ambient air guidelines developed from OELs.

As indicated previously, air quality guidelines used for the protection of acute health effects in humans are on the same order as concentrations for protecting vegetation. This indicates that human health-based criteria for ammonia may be adequate for protection of vegetation.

8.2 Chronic Exposure Conditions

The health effects following chronic inhalation exposure of animals include nasal irritation; inflammatory response in lungs; reduced olfactory acuity, and lethargy. Animal studies have also demonstrated that ammonia exposure can reduce immune response and increase susceptibility to bacterial infection of the respiratory tract. These types of effects have been observed in controlled animal studies at concentrations ranging from 40,000 to 1,100,000 $\mu g/m^3$ (58 to 1,590 ppm) over exposure durations ranging from 24 to 90 days continuously. Chronic effects reported in humans include reduction in pulmonary function; cough; phlegm; wheeze, and dyspnea. These types of effects have been observed at an estimated exposure concentration equivalent to 50 $\mu g/m^3$ (72 ppm) over one year of occupational exposure.

Numerous agencies have adopted levels ranging between 100 and 208 $\mu g/m^3$ (144 and 300 ppb) for chronic exposure conditions (e.g. US ATSDR, US EPA, Cal EPA). Both US ATSDR and US EPA used non-carcinogenic risk assessment procedures to develop their guidelines. Animal feedlot operations appear to be able to produce local ambient ammonia concentrations of a sufficient amount to be applicable to these types of guidelines. However it is unknown whether these amounts would be of a persistent (long-term) nature to be a public health concern.

Several agencies (Michigan DEQ and Washington DOE) have adopted the US EPA reference concentration (RfC) of 100 $\mu g/m^3$ (144 ppb) as a 24-hour guideline. As the RfC is more applicable to longer-term exposure conditions, the rationale of applying it to a 24-hour duration is questioned.

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APPENDICES

APPENDIX A

AMMONIA EMISSIONS (NPRI, 1999)

Table A-1: Total Emissions of Ammonia According to NPRI, 1999 (in tonnes, ranked by province and by total emissions)

NPRI ID	Company	City	Ammonia Emissions (tones)					
			Province	Air	Water	Land	Underground	Total
2134	Agrium Products Inc	Redwater/Municipal District Of Sturgeon	AB	2566 650	13.160	4 640	1441 630	4026.080
2960	Shell Canada Products Limited	Fort Saskatchewan	AB	0	0 170	0	2978 000	2978.170
3821	Canadian Fertilizers Limited	Medicine Hat	AB	2347 075	22.302	0	0	2369 377
3903	Petro-Canada	Edmonton	AB	0	0.565	0	1993.733	1994 298
3269	Agrium Inc.	Calgary	AB	1723 400	0	1.400	0	1724.800
4874	Agrium	Fort Saskatchewan	AB	498 400	0	0	1123 000	1621 400
2274	Syncrude Canada Ltd.	Fort McMurray	AB	1061 690	0	0	0	1061 690
3707	Imperial Oil	Edmonton	AB	0	0 462	0	861 285	861 747
2132	Sherritt International Corporation	Fort Saskatchewan	AB	441.219	57.828	0.165	0	499.212
5309	City Of Calgary - Wastewater & Drainage	Calgary	AB	0	352 000	0	0	352 000
5232	Lakeside Feeders Ltd.	Brooks	AB	0	0	338.000	0	338.000
4868	The Cobalt Refinery Company Inc.	Fort Saskatchewan	AB	203.522	14 945	0.018	0	218 485
5308	City Of Calgary - Wastewater & Drainage	Calgary	AB	0	211.000	0	0	211.000
0947	Rogers Sugar Ltd	Taber	AB	61 500	18 710	29 200	0	109 410
0223	Daishowa-Marubeni International	MD Of Northern Lights	AB	94.741	0	0	0	94 741
2282	Transalta Utilities Corporation	Wabamun	AB	94.000	0	0	0	94 000
2630	Johns Manville Canada Inc.	Innisfail	AB	73.413	0	0	0	73 413
2875	Weyerhaeuser Canada Ltd	Grande Prairie	AB	43 905	28 180	0	0	72 085
0001	Alberta-Pacific Forest Industries Inc.	Boyle	AB	54.385	6.307	0	0	60 692
1033	Atco Electric	Forestburg	AB	0	42.067	0	0	42 067
1251	Owens-Corning Canada Inc	Edmonton	AB	28.908	0.051	0	0	28 959
2749	City Of Medicine Hat	Medicine Hat	AB	0	21 590	1 160	0	22.750
4885	The Westaim Corporation	Fort Saskatchewan	AB	21.964	0	0	0	21 964
1175	Agrium	County Of Lacombe	AB	20 583	0	0	0	20 583
2857	Orica Canada Inc	Carseland	AB	20 100	0	0	0	20 100
5235	Cargill Foods	High River	AB	4 500	5.374	0.026	0	9.900
3758	Petro-Canada	Edson	AB	6 935	0	0	0	6 935
2316	Union Carbide Canada Inc	Red Deer	AB	0	4 870	0	0	4 870
0878	Millar Western Forest Products Ltd	Whitecourt	AB	0.158	4 050	0	0	4 208
0280	Dow Chemical Canada Incorporated	Fort Saskatchewan	AB	0	2.307	1.314	0	3.621

Table A-1: **Total Emissions of Ammonia According to NPRI, 1999 (in tonnes, ranked by province and by total emissions) (continued)**

NPRI ID	Company	City	Province	Ammonia Emissions (tonnes)				
				Air	Water	Land	Underground	Total
3959	Slave Lake Pulp	Slave Lake	AB	0	3.220	0	0	3.220
4884	Umex Inc	Leduc	AB	2 200	0	0	0	2 200
3910	Epcor Water Services	Edmonton	AB	0	1.897	0	0	1.897
3912	Epcor Water Services	Edmonton	AB	0	1 481	0	0	1.481
2230	Suncor Energy Inc.	Fort McMurray	AB	0	1 420	0	0	1.420
2376	Western Co-Operative Fertilizers Limited	Calgary	AB	1 183	0	0	0	1.183
1028	Alberta Newsprint Company	Whitecourt	AB	0	0 518	0	0	0 518
4721	Enerchem International Inc.	Nisku	AB	0	0	0	0	0 450
0011	Borden Chemical Canada Ltd	Edmonton	AB	0	0	0	0	0 425
4567	Nalco/Exxon Energy Chemicals Canada Inc	Nisku	AB	0.168	0	0	0	0 168
0853	Marsulex Inc.	Fort Saskatchewan	AB	0.100	0	0	0	0.100
5322	United Grain Growers	Camrose	AB	0	0	0	0	0.100
5321	United Grain Growers Limited	Vermilion	AB	0	0	0	0	0.100
5331	Untied Grain Growers Limited	Rycroft	AB	0	0	0	0	0 100
0250	Degussa Canada Ltd	Gibbons	AB	0	0 037	0	0	0.037
2183	Hci Stanchem Inc. (As55)	Leduc	AB	0	0	0	0	0 029
2128	Shell Canada Limited	Peace River	AB	0.002	0 002	0 004	0	0.008
5715	Hci Stanchem Inc. (Aw10)	Leduc	AB	0	0	0	0	0 001
5307	City Of Calgary - Wastewater & Drainage	Calgary	AB	0	0	0	0	0
4867	Burns Philp Food Limited	Calgary	AB	0	0	0	0	0
1782	Methanex Corporation	Medicine Hat	AB	0	0	0	0	0
3088	Rw Packaging Ltd.	Edmonton	AB	0	0	0	0	0
5284	Talisman Energy Inc	Edson	AB	0	0	0	0	0
3802	Cominco Ltd	Trail	BC	250	152.000	0	0	402 000
2377	Western Pulp Limited Partnership	Port Alice	BC	0	271 000	0	0	271.000
2924	Weyerhaeuser Company Limited	Kamloops	BC	80	189.900	0	0	269.900
0333	Fletcher Challenge Canada	Campbell River	BC	0	186.000	0	0	186.000
1797	Canadian Forest Products Ltd.	Prince George	BC	99 356	64.240	0	0	163.596
1266	Fletcher Challenge Canada	Crofton	BC	70.800	60	0	0	130.800

Table A-1: **Total Emissions of Ammonia According to NPRI, 1999 (in tonnes, ranked by province and by total emissions) (continued)**

NPRI ID	Company	City	Province	Ammonia Emissions (tonnes)				
				Air	Water	Land	Underground	Total
1383	Pope & Talbot Ltd	Nanaimo	BC	70.120	27 106	0	0	97.226
1419	Howe Sound Pulp And Paper Limited	Port Mellon	BC	51 801	19.967	0	0	71.768
1185	Crestbrook Forest Industries	Skookumchuck	BC	20 500	5 600	0	0	26.100
3907	Cominco Ltd.	Kimberley	BC	0	24.071	0 612	0	24 683
0723	Pacifica Papers Inc	Powell River	BC	13 650	6.680	0	0	20 330
4063	Canfor	Prince George	BC	0	17 500	0	0	17 500
3240	B C Hydro	Port Moody	BC	15 100	0	0	0	15 100
5106	Domtar Inc	Delta	BC	11 657	0	0	0	11 657
1593	Pacifica Papers	Port Alberni	BC	0	10 822	0	0	10 822
5104	Pacific Ammonia Inc	Vancouver	BC	5.405	1 340	0	0	6.745
2553	Quesnel River Pulp Company	Quesnel	BC	0	4 900	0	0	4.900
5105	Donohue Forest Products Inc	Mackenzie	BC	0	1.700	0	0	1.700
3374	Crown Packaging Ltd	Burnaby	BC	0	1.600	0	0	1 600
1257	Fibreco Pulp A Division Of Slocan Forest Products Ltd	Taylor	BC	0	1 248	0	0	1.248
0394	Homestake Canada Inc	Above Hedley	BC	0	0 030	0	0	0.030
0013	Borden Chemical Canada Ltd	Vancouver	BC	0	0	0	0	0 027
5773	Hci Stanchem Inc. (Bs08)	Langley	BC	0 004	0	0	0	0 004
2776	Chevron Canada Limited	Burnaby	BC	0	0	0	0	0
5101	Gemini Packaging Ltd.	Richmond	BC	0	0	0	0	0
4308	Molson Canada	Vancouver	BC	0	0	0	0	0
2515	Simplot Canada Limited	Brandon	MB	974 160	6.600	16 900	0	997.660
2051	Tolko Manitoba	The Pas	MB	70 795	0 531	0	0	71 326
3414	Hudson Bay Mining And Smelting Company Ltd	Flin Flon	MB	0	13 780	0	0	13 780
5221	Western Cooperative Fertilizers Limited	Brandon	MB	7 018	0	0	0	7 018
5328	United Grain Growers Limited	Fannystelle	MB	0	0	0	0	0 100
5329	United Grain Growers Limited	Westbourne	MB	0	0	0	0	0.100
5327	United Grain Growers Limited	Souris	MB	0	0	0	0	0.100

Table A-1: **Total Emissions of Ammonia According to NPRI, 1999 (in tonnes, ranked by province and by total emissions) (continued)**

NPRI ID	Company	City	Province	Ammonia Emissions (tonnes)				
				Air	Water	Land	Underground	Total
2097	The Seagram Company Limited	Gimli	MB	0	0	0	0	0
5317	Maple Leaf Foods	Brandon	MB	0	0	0	0	0
1221	Fraser Papers Inc (Canada)	Edmundston	NB	0.225	199 900	0	0	200 125
3350	Mccain Foods (Canada)	Florenceville	NB	15.000	131.000	0	0	146 000
1617	Repap New Brunswick Inc	Miramichi	NB	44.600	60.900	0	0	105.500
2181	St Anne-Nackawic Company Ltd.	Nackawic	NB	24.710	42.930	0	0	67.640
2604	Irving Pulp & Paper Limited / Irving Tissue Company	Saint John	NB	49 370	0	0	0	49 370
5008	Av Cell Inc	Atholville	NB	0	39 110	0	0	39.110
4101	Irving Oil Limited	Saint John	NB	0	25.715	0	0	25 715
3394	Irving Paper	Saint John	NB	0 225	15.980	0	0	16.205
4876	Bowater Maritimes Inc	Dalhousie	NB	0 225	9.530	0	0	9.755
1572	J. D Irving Ltd	Utopia	NB	0 080	9 081	0	0	9 161
4890	Moosehead Breweries Limited	Saint John	NB	2 951	0	0	0	2 951
5006	Woodchem Canada Ltd	St Stephen	NB	0	0	0	0	0.100
4842	Flakeboard Company Limited	St. Stephen	NB	0	0	0	0	0
4316	North Atlantic Refining Ltd	Come By Chance	NF	0	1 191	0	0	1 191
4844	Bowater Inc	Liverpool	NS	0.225	56 700	0	0	56 925
3698	Imperial Oil	Dartmouth	NS	1.210	4 087	0	0	5 297
2221	Stora Enso	Port Hawkesbury	NS	0.225	0	0	0	0 225
4221	Miramar Giant Mine Limited	Yellowknife	NT	0	11 552	0	0	11 552
2548	Miramar Con Mine Ltd	Yellowknife	NT	0	6.310	0	0	6.310
4568	Canzinco Ltd	Nanisivik	NT	0	0.119	0	0	0.119
2240	City Of Toronto	Toronto	ON	0	2936.695	0	0	2936.695
0770	Regional Municipality Of Ottawa-Carleton	Gloucester	ON	0	1997 000	0	0	1997 000
1290	General Chemical Canada Ltd	Amherstburg	ON	1885 000	97 000	0	0	1982 000
3807	Nitrochem Corp. (Formerly Hydro Agri Canada L P)	Maitland	ON	1109 000	8 350	0	0	1117.350
2233	Terra International Canada Inc.	Courtright	ON	637 450	22.071	0	0	659.521
2238	City Of Toronto	Toronto	ON	0	621.000	0	0	621.000

Table A-1: **Total Emissions of Ammonia According to NPRI, 1999 (in tonnes, ranked by province and by total emissions) (continued)**

NPRI ID	Company	City	Province	Ammonia Emissions (tonnes)				
				Air	Water	Land	Underground	Total
3677	Regional Municipality Of Niagara	Niagara Falls	ON	0	171.630	0	0	171.630
4435	City Of Toronto	Toronto	ON	0	147.947	0	0	147.947
2984	Stelco Inc	Hamilton	ON	61 200	68 900	0	0	130 100
0928	Weyerhaeuser Company Limited	Dryden	ON	47.470	61 531	0	0	109.001
5614	Regional Municipality Of Niagara	Welland	ON	0	105 870	0	0	105 870
2607	Kimberly-Clark Corporation	Terrace Bay	ON	101 200	0	0	0	101 200
1465	Inco Limited	Copper Cliff	ON	0	92 564	0	0	92 564
3713	Dofasco Inc.	Hamilton	ON	75.860	12 800	0	0	88 660
3683	Regional Municipality Of Niagara	St Catharines	ON	0	82.050	0	0	82 050
1197	Domtar Papers	Cornwall	ON	61.600	19 311	0	0	80.911
3680	Regional Municipality Of Niagara	St Catharines	ON	0	73 620	0	0	73 620
3013	Norampac Inc	Red Rock	ON	52 720	20.440	0	0	73 160
3185	Domtar Inc.	Espanola	ON	69 030	3.660	0	0	72 690
1944	Bayer Inc	Sarnia	ON	67.140	2 250	0	0	69.390
1870	Paperboard Industries Corporation	Toronto	ON	61 610	0	0	0	61 610
2068	Rothsay, Member Of Maple Leaf Foods	Maryborough Township	ON	54 500	0.726	4.551	0	59 777
1207	Dupont Canada Inc.	Maitland	ON	31 410	21.458	0	0	52 868
3701	Imperial Oil	Nanticoke	ON	48.160	3.631	0	0	51.791
1070	Algoma Steel Inc	Sault Ste Marie	ON	21.572	22 093	0	0	43.665
0930	Bowater Pulp And Paper Canada Inc.	Thunder Bay	ON	10 720	30 890	0	0	41 610
4743	City Of London	London	ON	0	37 688	0	0	37 688
0462	Marathon Pulp Inc	Marathon	ON	12 336	21 953	0	0	34 289
2815	Falconbridge Ltd-Kidd Metallurgical Div	District Of Cochrane	ON	7.870	26 385	0	0	34.255
1941	Placer Dome (Cla) Limited	South Porcupine	ON	0	31.514	0	0	31 514
1857	Ottawa Fibre Inc	Ottawa	ON	30 450	0	0	0	30.450
3855	Lake Erie Steel Company	Nanticoke	ON	29 194	0.541	0	0	29.735
0917	Abitibi-Consolidated Incorporated	Fort Frances	ON	8 550	21 120	0	0	29 670
0775	Donohue Forest Products Inc.	Thorold	ON	0	25.200	0	0	25 200
3197	Williams Operating Corporation	Marathon	ON	0	23.500	0	0	23 500
1596	Tembec Industries Inc.	Smooth Rock Falls	ON	0	22.000	0	0	22.000

Table A-1: **Total Emissions of Ammonia According to NPRI, 1999 (in tonnes, ranked by province and by total emissions) (continued)**

NPRI ID	Company	City	Province	Ammonia Emissions (tonnes)				
				Air	Water	Land	Underground	Total
5687	Roxul, Inc.	Milton	ON	21 000	0	0	0	21.000
5612	Regional Municipality Of Niagara	Grimsby	ON	0	20 210	0	0	20 210
1400	Battle Mountain Canada Ltd	Marathon	ON	0	20.107	0	0	20 107
3163	Ontario Power Generation Inc	Bowmanville	ON	18.000	2 000	0	0	20
4755	City Of Windsor	Windsor	ON	0	19.488	0	0	19 488
5656	Placer Dome Canada	Thunder Bay	ON	5 300	12 880	0	0	18 180
1980	Domtar Inc	Ottawa	ON	0	17.901	0	0	17.901
4419	Timminco Limited	Haley	ON	0	17.447	0	0	17.447
3161	Ontario Power Generation Inc	Pickering	ON	14 000	2.000	0	0	16.000
1233	Falconbridge Limited	Onaping	ON	0	15 799	0	0	15 799
1199	Panolam Industries Ltd	Stephenson Township	ON	15 500	0	0	0	15 500
1245	Owens-Corning Canada	Scarborough	ON	14.944	0	0	0	14 944
4036	Placer Dome Canada (Cla) Limited	Timmins	ON	0	14.770	0	0	14.770
1882	Fibrex Insulations Inc	Sarnia	ON	13 080	0	0	0	13.080
4466	Brake Pro Ltd	Concord	ON	12.604	0	0	0	12.604
1935	Placer Dome (Cla) Limited	Balmertown	ON	0	11.900	0	0	11 900
0776	Reckitt & Colman Plc	Toronto	ON	11.600	0	0	0	11 600
4484	Bauer Industries Ltd	Waterloo	ON	10 260	0	0	0	10 260
4756	Long Manufacturing Ltd	Oakville	ON	10 054	0	0	0	10.054
5251	Praxair Canada Inc	Maitland	ON	9.870	0	0	0	9.870
0201	City Of Peterborough W W T P.	Peterborough	ON	0	9 025	0	0	9 025
1145	Cameco Corporation - Port Hope Facility	Port Hope	ON	8.794	0 038	0	0	8 832
1947	Port Colborne Poultry Ltd	Port Colborne	ON	3 957	2.233	2 476	0	8.666
0319	Eti Canada Inc.	North Bay	ON	0	1.100	7 200	0	8 300
5252	Praxair Canada Inc	Sarnia	ON	7.981	0	0	0	7.981
1568	Kinross Gold Corporation	Kirkland Lake	ON	0	7 597	0	0	7 597
5705	Alpine Plant Foods Corporation	Baden	ON	7 000	0	0	0	7.000
3071	Sunoco Inc	Sarnia	ON	0	6.440	0	0	6 440
2070	Vft Inc.	Hamilton	ON	6 110	0	0	0	6 110
3808	Ontario Power Generation Inc.	Mun. Of Bruce-Tiverton	ON	4.000	2.000	0	0	6.000

Table A-1: Total Emissions of Ammonia According to NPRI, 1999 (in tonnes, ranked by province and by total emissions) (continued)

NPRI ID	Company	City	Province	Ammonia Emissions (tonnes)				
				Air	Water	Land	Underground	Total
5613	Regional Municipality Of Niagara	Fort Erie	ON	0	5.700	0	0	5.700
3090	Dynamic & Proto Circuits Inc.	Stoney Creek	ON	5.600	0	0	0	5.600
1054	Albright & Wilson Americas Limited	Port Maitland	ON	4.991	0	0	0	4.991
2216	Stepan Canada Inc	Longford Mills	ON	4.869	0	0	0	4.869
1684	Neste Resins Canada	Thunder Bay	ON	4.562	0	0	0	4.562
5750	Glendale International Corp.	Scarborough	ON	3.980	0	0	0	3.980
3962	Shell Canada Products Ltd	Corunna	ON	0.986	2.856	0	0	3.842
2869	Teck-Corona Operating Corporation	Marathon	ON	0	2.970	0	0	2.970
3704	Imperial Oil	Sarnia	ON	2.167	0.551	0	0	2.718
5659	Georgia Pacific Canada	Thorold	ON	0	2.470	0	0	2.470
2322	Uniroyal Chemical Company	Elmira	ON	2.094	0.005	0	0	2.099
5608	Pc World	Scarborough	ON	1.998	0	0	0	1.998
1861	Ontario Power Generation Inc.	Nanticoke	ON	0.503	1.397	0	0	1.900
5762	Oxy Vinyls Canada Inc.	Thorold	ON	0	1.757	0	0	1.757
1993	Coretec Inc.	Scarborough	ON	1.588	0	0	0	1.588
2065	Rohm And Haas Canada Inc	West Hill	ON	1.033	0	0	0	1.033
0494	Chinook Group Limited	Sombra	ON	0.104	0.905	0	0	1.009
4502	Coretec Inc.	Scarborough	ON	0	0	0	0	0.766
5739	Commercial Alcohols Inc	Chatham	ON	0.670	0	0	0	0.670
3901	Petro-Canada	Oakville	ON	0.071	0.562	0	0	0.633
1809	Ontario Power Generation Inc.	Courtright	ON	0.464	0.079	0	0	0.543
2891	Jempak Canada Inc	Oakville	ON	0.337	0	0	0	0.337
5797	Toledo Techologies	Guelph	ON	0.300	0	0	0	0.300
0009	Borden Chemical Canada Ltd.	North Bay	ON	0	0	0	0	0.248
0981	Abitibi-Consolidated Inc	Thunder Bay	ON	0	0.240	0	0	0.240
3899	Petro-Canada	Mississauga	ON	0	0.185	0	0	0.185
0978	Abitibi-Consolidated Inc	Iroquois Falls	ON	0	0.103	0.009	0	0.112
0488	Casco Inc.	Cardinal	ON	0	0	0	0	0.100
0485	Casco Inc.	London	ON	0	0	0	0	0.100
0459	Intergen Biomanufacturing Corporation	Toronto	ON	0.100	0	0	0	0.100

Table A-1: Total Emissions of Ammonia According to NPRI, 1999 (in tonnes, ranked by province and by total emissions) (continued)

NPRI ID	Company	City	Province	Ammonia Emissions (tonnes)				
				Air	Water	Land	Underground	Total
0679	Chembond Limited	Brampton	ON	0.100	0	0	0	0.100
4899	Deluxe Toronto	Toronto	ON	0	0	0	0	0.100
1687	Neste Resins Canada	North Bay	ON	0	0	0	0	0.100
3520	Cxy Chemicals Canada Limited Partnership	Amherstburg	ON	0	0	0	0	0.100
3657	Cameco Corporation	Blind River	ON	0	0	0	0	0.100
2695	Casco Inc	Port Colbrone	ON	0	0	0	0	0.100
5772	Hci Stanchem Inc (Ow06)	Cornwall	ON	0	0	0	0	0.082
4759	Maratek Environmental Inc	Bolton	ON	0.053	0	0	0	0.053
0711	Flint Ink Corporation	Concord	ON	0.050	0	0	0	0.050
2626	Collins & Aikman	Kitchener	ON	0.050	0	0	0	0.050
3146	Dow Chemical Canada Inc.	Sarnia	ON	0	0	0	0	0.012
1109	Atotech Canada Ltd.	Burlington	ON	0.009	0	0	0	0.009
5852	Union Carbide Canada Inc	Sarnia	ON	0	0	0	0	0.003
3923	City Of Toronto	Toronto	ON	0	0	0	0	0
4560	Electrical Contacts Limited	Hanover	ON	0	0	0	0	0
0125	Atlantic Packaging Products Ltd.	Whitby	ON	0	0	0	0	0
4437	Lightning Circuits Inc.	Niagara On The Lake	ON	0	0	0	0	0
3919	City Of Toronto	Toronto	ON	0	0	0	0	0
0064	B&W Heat Treating (1975) Ltd	Kitchener	ON	0	0	0	0	0
3686	Regional Municipality Of Niagara	Port Colborne	ON	0	0	0	0	0
1093	Armstrong Corporation	Mississauga	ON	0	0	0	0	0
4754	Region Of Ottawa Carleton	Ottawa	ON	0	0	0	0	0
5625	Safety-Kleen Ltd	Thorold	ON	0	0	0	0	0
4771	Regional Municipality Of Halton	Burlington	ON	0	0	0	0	0
3921	City Of Toronto	Toronto	ON	0	0	0	0	0
1531	J M Schneider Inc	Kitchener	ON	0	0	0	0	0
3805	Ontario Clean Water Agency	Mississauga	ON	0	0	0	0	0
3422	Dupont Canada Inc.	Kingston	ON	0	0	0	0	0
5688	Atlantic Packaging Products Ltd	Scarborough	ON	0	0	0	0	0
4045	Stelwire Ltd.	Hamilton	ON	0	0	0	0	0

Table A-1: **Total Emissions of Ammonia According to NPRI, 1999 (in tonnes, ranked by province and by total emissions) (continued)**

NPRI ID	Company	City	Province	Ammonia Emissions (tonnes)				
				Air	Water	Land	Underground	Total
4433	Wood Wyant Inc	Toronto	ON	0	0	0	0	0
5632	Perth Soap Inc	Perth	ON	0	0	0	0	0
3227	General Motors Of Canada Ltd	St Catharines	ON	0	0	0	0	0
3971	Morton International, Ltd	Ajax	ON	0	0	0	0	0
5828	Aventis Pasteur Limited	Toronto	ON	0	0	0	0	0
4728	Region Of Ottawa Carleton	Ottawa	ON	0	0	0	0	0
1464	Imperial Oil	Sarnia	ON	0	0	0	0	0
5790	City Of London	London	ON	0	0	0	0	0
4875	Cavendish Farms	New Annan	PE	0	1 160	0	0	1 160
0099	Les Mines Agnico-Eagle	Cadillac	QC	0	131 000	0	0	131 000
0879	Barrick Gold Corporation	Malartic	QC	0	110 462	0	0	110 462
3140	Cartons St-Laurent Inc	La Tuque	QC	73 088	36 374	0	0	109.462
5480	Les Industries Paperboard International Inc	Jonquière	QC	101.025	6.800	0	0	107.825
2001	Produits Forestiers Donohue Inc	Baie-Comeau	QC	0 225	101 400	0	0	101.625
3242	Produits Forestiers Donohue Inc	St-F,Licien	QC	40	45.000	0	0	85 000
2948	Tembec Inc.	T,Miscaming	QC	10.200	74.100	0	0	84 300
2502	Abitibi-Consolidated	Trois-Rivióres	QC	10.200	44 690	0	0	54 890
2636	Abitibi- Consolidated Inc	La Baie	QC	0	54 400	0	0	54 400
0271	Emballages Smurfit-Stone Canada Inc	Portage-Du-Fort	QC	30 653	21 108	0	0	51.761
1528	Industries James Maclaren Inc	Thurso	QC	36 500	11.745	1.095	0	49.340
1195	Papier De Communication Domtar	Windsor	QC	47 320	0.020	0	0	47 340
3292	Emballages Stone (Canada) Inc.	New Richmond	QC	28 846	12.133	0	0	40.979
0929	Bowater Pulp And Paper Canada Inc.	Gatineau	QC	0	34.010	0	0	34 010
1143	Cambior	Amos	QC	0	25 728	0	0	25 728
3124	Viasystems Canada Inc.	Granby	QC	25.104	0	0	0	25.104
5464	Corporation Minière Inmet, Division Troilus	Chibougamau	QC	0	23 000	0	0	23 000
3897	Petro-Canada	Montreal	QC	0	22 870	0	0	22 870
4340	La Compagnie Gasp,Sia Lt,E	Chandler	QC	0.127	22.200	0	0	22 327
0279	Domtar Inc	Lebel-Sur-Qu,Villon	QC	12 300	7 700	0	0	20
1525	Papier Masson Limit,E	Masson-Angers	QC	0	19.400	0	0	19.400

Table A-1: **Total Emissions of Ammonia According to NPRI, 1999 (in tonnes, ranked by province and by total emissions) (continued)**

NPRI ID	Company	City	Province	Ammonia Emissions (tonnes)				
				Air	Water	Land	Underground	Total
1608	Cambior Inc	Mont Brun	QC	0	14.060	0	0	14.060
0983	Abitibi-Consolidated Inc.	Alma	QC	0.483	13 439	0 024	0	13 946
3928	Ultramar Lt,E	St-Romuald	QC	1.285	10.474	0	0	11.759
3875	Cascades East Angus Inc.	East Angus	QC	11 700	0	0	0	11 700
2989	Uniboard Canada Inc.	Sayabec	QC	10.507	0	0	0	10.507
0987	Abitibi-Consolidated Inc	Beaupr,	QC	0	10.100	0	0	10.100
4919	Uniforet Inc	Port-Cartier	QC	0	9.007	0	0	9 007
1858	Owens-Corning Canada Inc	Candiac	QC	8.753	0	0	0	8.753
3828	Donohue Inc.	Amos	QC	0	6.200	0.750	0	6 950
3127	Produits Shell Canada Limit,E	Montr,Al	QC	1 800	4 590	0	0	6 390
2935	Les Mines Mcwatters Inc	Dubuisson	QC	0	5 121	0	0	5 121
3276	Les Mines Mcwatters Inc	Val-D'or	QC	0	4.827	0	0	4 827
3125	Viasystems Canada Inc.	Kirkland	QC	3 795	0	0	0	3.795
5403	Acton International Inc.	Acton Vale	QC	2 300	0	0	0	2 300
0979	Abitibi Consolidated	Jonquišre	QC	0	1.900	0.100	0	2 000
4870	Cxy Chemicals Canada Limited Partnership	Beauharnois	QC	0	1 600	0	0	1.600
4788	Tembec Matane Inc.	Matane	QC	0	0 417	0	0	0.417
5455	Services Safety-Kleen (Qu,Bec) Lt,E	Thurso	QC	0 400	0	0	0	0 400
1681	Neste Resins Canada	Ste Therese	QC	0 318	0	0	0	0 318
5438	Cosmair Canada Inc.	Ville Saint-Laurent	QC	0 200	0	0	0	0 200
2996	Rhodia Canada Inc	Salaberry-De-Valleyfield	QC	0	0	0	0	0 144
4392	Metcor Inc	St-Eustache	QC	0	0	0	0	0.130
0938	Boehme Filatex Canada Inc	St-Jean-Sur-Richelieu	QC	0	0	0	0	0.100
0729	Mapei Inc	Laval	QC	0	0	0	0	0 100
5775	Hci Stanchem Inc (Qr59)	Ville Ste-Catherine	QC	0 006	0	0.056	0	0 062
0007	Borden Chemical Canada Ltd	Laval	QC	0	0	0	0	0.055
0281	Dow Chemical Canada Inc	Varennes	QC	0 026	0	0	0	0 026
1648	Solutia Canada Inc	Lasalle	QC	0 008	0	0	0	0 008
0105	Aldex Chemical Co. Ltd	Granby	QC	0	0	0	0	0 001
0705	Lallemand Inc	Montr□Al	QC	0	0	0	0	0

Table A-1: **Total Emissions of Ammonia According to NPRI, 1999 (in tonnes, ranked by province and by total emissions) (continued)**

NPRI ID	Company	City	Province	Ammonia Emissions (tonnes)				
				Air	Water	Land	Underground	Total
3395	Les Poudres Metalliques Du Quebec Ltee	Tracy	QC	0	0	0	0	0
4888	Les Produits Chimiques Bgr Inc	Pointe-Claire	QC	0	0	0	0	0
4945	Produits Chimiques Regent Lt,E	Vaudreuil-Dorion	QC	0	0	0	0	0
2791	Dyno Nobel Ltd, Mont-Wright	Fermont	QC	0	0	0	0	0
0252	Dural Div Multibond.	Dorval	QC	0	0	0	0	0
4932	Aliments Bums Philp Limite	Lasalle	QC	0	0	0	0	0
2957	Tembec Inc.	T,Miscaming	QC	0	0	0	0	0
4931	Textile Rubber & Chemical Canada (Ltd)	St-Jean-Sur-Richelieu	QC	0	0	0	0	0
4322	Peinture Denalt Lt,E	St-L,Onard	QC	0	0	0	0	0
4338	Domfer Poudres Metalliques Ltee	Lasalle	QC	0	0	0	0	0
1801	Hydro Agri Canada S E C	Ste-Rosalie	QC	0	0	0	0	0
4361	Kraft Canada Inc.	Mont-Royal	QC	0	0	0	0	0
2077	Saskferco Products Inc	Belle Plaine	SK	761 700	0	0	0	761 700
3610	Weyerhaeuser Saskatchewan Limited	Prince Albert	SK	56 900	23.700	0	0	80 600
1148	Cameco Corporation	Saskatoon	SK	8 500	27 290	0	0	35.790
3348	Cogema Resources Inc.	Saskatoon	SK	1 244	16.187	0	0	17 431
1147	Cameco Corporation Ltd	Saskatoon	SK	0	14.580	0	0	14 580
4048	Consumers' Co-Op Ref Ltd	Regina	SK	7 329	0	0	0	7 329
3977	Akzo Nobel Chemicals Ltd.	Saskatoon	SK	1.300	3 495	0	0	4 795
5324	United Grain Growers Limited	Melville	SK	0	0	0	0	0 100
5323	United Grain Growers Limited	Valparaiso	SK	0	0	0	0	0 100
5330	United Grain Growers Limited	Rosthern	SK	0	0	0	0	0 100
5326	United Grain Growers Limited	Canora	SK	0	0	0	0	0 100
5325	United Grain Growers Limited	Dixon	SK	0	0	0	0	0 100
0409	Husky Oil Operations	Lloydminster	SK	0 009	0	0	0 006	0 015
4194	National Manufacturing Of Canada Inc	Swift Current	SK	0	0	0	0	0
1510	International Minerals & Chemical (Canada) L	Esterhazy	SK	0	0	0	0	0
1513	International Minerals & Chemical (Canada)	Esterhazy	SK	0	0	0	0	0
4951	Viceroy Minerals Corporation	Dawson City	YT	0	0	0	0	0.014

APPENDIX B

AIR SAMPLING AND ANALYTICAL METHODS

Appendix B: Air Sampling and Analytical Methods

B-1 Reference Methods

Air sampling and monitoring methods and technologies for ammonia used in practice by jurisdictions and established agencies are reported. In general, standard air monitoring methods and technologies for ammonia involve pump-and-tube sampling approaches using short-term detector tubes with a variety of subsequent analytical approaches. These techniques are more suited for personal, occupational and area monitoring than for ambient monitoring. Therefore, other methods should be used to determine long-term ambient ammonia concentrations since tubes offer only spot checks of the local environment.

Widely employed and accepted referenced air monitoring methods and technologies for ammonia have been developed, tested and reported by the National Institute of Occupational Safety and Health (NIOSH) and Occupational Safety and Health Administration (OSHA). Additional methods are currently used in practice by many jurisdictions and established agencies but are not considered standard methods and are discussed in the next section.

The NIOSH currently has two methodologies for the determination of ammonia in air. NIOSH Method 6015 consists of collecting ammonia on sulfuric acid-treated silica gel, desorbing with deionized water, and analyzing by visible absorption spectrophotometry (NIOSH, 1994). Sampling is conducted by drawing a known volume of air through a solid sorbent tube containing sulfuric acid-treated silica gel (200 milligrams (mg) in the front section and 100 mg in the back section) using a personal sampling pump calibrated to the suggested flow rate. In addition, a prefilter may be used to remove particulate interferences. A suggested flow rate of 0.1 to 0.2 liters per minute (L/min) is used to collect a total volume of between 0.1 and 96 L. The working ammonia concentration range for this technique is 0.2 to 400 parts per million by volume (ppmv) (0.15 to 300 mg/m^3) for a 10 L sample.

The second NIOSH method serves as an alternative analytical procedure to the automated spectrophotometric procedure of Method 6015. NIOSH Method 6016 consists of collecting ammonia on sulfuric acid-treated silica gel, desorbing with deionized water, and analyzing by ion chromatography with conductivity detection (NIOSH, 1996). Sampling is conducted by drawing a known volume of air through a solid sorbent tube containing sulfuric acid-treated silica gel (200 mg in the front section and 100 mg in the back section) using a personal sampling pump calibrated to the suggested flow rate. A prefilter may be used to remove particulate interferences. A suggested flow rate of 0.1 to 0.5 L/min is used to collect a total volume of between 0.1 L and 96 L. The working ammonia concentration range for this technique is 24 to 98 ppmv (17 to 68 mg/m^3) for a 30 L sample.

The current methodology used by OSHA to determine ammonia in air (OSHA Method 188) consists of using a personal sampling pump to draw a known volume of air through a glass tube containing carbon beads impregnated with sulfuric acid (OSHA, 1991; Bishop et al., 1986). Ammonia is collected and converted to ammonium sulphate. The sample is then desorbed with deionized water and analyzed as ammonium ion using ion chromatography. This method replaces the previous OSHA sampling procedure for ammonia that involved the use of a midget fritted glass bubbler containing 0.1 N sulphuric acid and subsequent analysis by a gas-specific electrode. The advantages of this current method include: adequate sensitivity for determining compliance with the OSHA permissible exposure limit (PEL) for workplace exposures to ammonia; simple, rapid and easily automated; specific for ammonium ion; potential exposure to H_2SO_4 is reduced; and after sample preparation, ammonia can also be determined by other analytical procedures. The disadvantages of this method include positive interferences from ammonium salts present in the air and from monoethanolamine, isopropanolamine or propanolamine (which if present will produce peaks in the vicinity of the ammonium ion when using this method).

Sampling is conducted by drawing of air through a glass tube containing carbon beads (500 mg in the front section and 250 mg in the back section) impregnated with sulfuric acid using a personal sampling pump calibrated to within ±5% of the recommended flow rate. The suggested flow rate is 0.10 L/min (for TWA (time weighted average) determinations) and 0.5 L/min (for STEL (short-term exposure limit) determinations). The suggested volume collected is 24 L (TWA determinations) and 7.5 L (STEL determinations). The reliable qualitative detection limit of the overall procedure is 0.60 ppmv for a 24 L sample and 1.9 ppmv for a 7.5 L sample. The reliable quantitative detection limit of the overall procedure is 1.5 ppmv (1 mg/m^3) for a 24 L sample and 4.8 ppmv (3.3 mg/m^3) for a 7.5 L sample. These high levels render this method unsuitable for ambient monitoring situations.

B-2 Alternative, Emerging Technologies

Filter pack

Time-integrated atmospheric ammonia measurements are most commonly carried out by filter packs or annular denuder methods. The filter pack method is based on separating the particle phase and unwanted gaseous components of sampled air through filtration and absorbing ammonia gas passing through the filter in an acid medium (Ferm et al., 1988; Harrison and Kitto, 1990; Andersen and Hovmand, 1994). This process allows the collection of both particle ammonium (NH_4^+) and gaseous ammonia (NH_3). Since it is a preconcentration technique, it also allows for the sampling of ammonia at very low concentrations. Usually the filter pack has an open face and consists of a series of filters including: a 47-millimeter (mm) Teflon filter with a pore size of 2 micrometers (μm) for the collection of atmospheric particles, a 47-mm Nylasorb nylon filter with a pore size of 1 μm for the collection of HNO_3, and a cellulose filter impregnated with citric acid (or oxalic acid) for the collection of NH_3.

Ambient air is typically drawn into the filter pack at a rate of 19 liters per minute (L/min) by a vacuum pump. After sampling, filters are extracted in a 20-milliliter (mL) solution of deionized water and the extracts are analyzed on anions using ion chromatography and on NH_4^+ using a colorimetric method (Nessler, fluorescence, indophenol or pyridine-pyrazolone techniques). Given the NH_4^+ concentration in the extract, the flow rate of air through the filter pack and the sampling duration, the average atmospheric ammonia concentration can be calculated.

It has been reported that the collection efficiencies of filter packs are generally lower than that of other collection techniques due to the absorption of ammonia on acidic particulates collected and removed by the Teflon prefilter (Allegrini et al., 1987). Overestimation of ammonia concentrations can also occur due to the possible volatile loss of ammonium salts from the Teflon filter with subsequent collection as gaseous ammonia. In addition, the system requires sample times in the order of 2 hours or longer (to achieve a detection limit of 0.036 ppbv (0.025 $\mu g/m^3$)) and is somewhat labour intensive (Ferm et al., 1988). On the other hand, the system is reasonably simple and portable and equipment costs are modest.

Annular denuder

An approach used to avoid the problems of positive and negative chemical artifacts experienced by the filter pack technique while still achieving a similar detection limit is the use of annular denuder systems (Ferm, 1979; Allegrini et al., 1987; Ferm et al., 1988; Koutrakis et al., 1989; Harrison and Kitto, 1990; Andersen and Hovmand, 1994; Sioutas et al., 1996). The denuder method is based on the difference in diffusion velocity of gases compared to particles. A laminar air stream is pumped through a glass tube coated with a sorbent suitable for the gas in question. The gas diffuses to the wall of the tube while the particles pass the tube with the airflow and are impacted on a backing filter pack system.

The non-automatic annular denuder system normally consists of an impactor or cyclone (2.5 µm 50% cutoff diameter) connected to a least one set of parallel denuder tubes (glass tubes normally being 25 centimeters (cm) long and 1.0 cm in internal diameter). Each set consists of two Na_2CO_3 coated annular denuders for collection of SO_2, HNO_2 and HNO_3, a citric acid (or oxalic acid) coated annular denuder for collection of NH_3, and a filter pack containing a 47-mm Teflon filter with a pore size of 2 µm for the collection of particles followed by a 47-mm Nylasorb nylon filter with a pore size of 1 µm for the collection of HNO_3 released from the Teflon filter due to dissociation of ammonium nitrate.

The system is enclosed in a box and connected to a vacuum pump with flow and time controller. The flow rate is typically 16.7 L/min. After sampling, denuders and filters are extracted in a 20 mL solution of deionized water and the extracts are analyzed on anions using ion chromatography and on NH_4^+ using a colorimetric method (Nessler, fluorescence, indophenol or pyridine-pyrazolone techniques). Given the NH_4^+ concentration in the extract, the flow rate of air through the tube and the sampling duration, the average atmospheric ammonia concentration can be calculated. This technique is very labour intensive (coating, drying, washing, analyzing, and re-coating procedures), requires many manipulations for a single measurement and fine time resolution is not possible. However, equipment requirements and costs are modest making it an attractive option for routine deployment in the field.

Passive monitoring

The rapid development of passive monitors based on diffusion has resulted in new time-integrated methods for sampling ammonia. Application of passive sampling has long been a tradition in workplace air monitoring and several methods for the determination of ammonia have been developed (Frenzel et al., 1995; Thijsse et al., 1998; Kirchner et al., 1999). Despite the advantages that passive sampling methods have to offer (i.e. they are cheap, simple to use, able to provide high spatial resolution, do not require power supplies, can be used to assess long-term concentrations and are well-suited for remote area measurements) they have generally not been used for ambient monitoring. This can mainly be attributed to the only reasonable time resolution being available when low-level contaminants are present.

There are basically two types of passive samplers to distinguish: the tube type and the badge type. For the tube type, the diffusion is determined through a static air column. Diffusion processes can be calculated according to Fick's first law of diffusion provided that the diffusion coefficient is known, as in the case of ammonia. For the badge type, the permeation processes can also be described by Fick's first law of diffusion. In this case the diffusion is determined by a static layer of air and a membrane of defined pore size. The collection rate is analogous to that of the tube type sampler (Kirchner, 1999).

The tube type passive monitoring method for the determination of atmospheric levels of ammonia is based on the collection of ammonia at the phosphoric acid (Frenzel et al., 1995) or oxalic acid (Schjoerring et al., 1992) coated bottom of small glass vials and subsequent flow injection analysis of the trapped ammonium. The procedure involves fixation of the samplers at the measuring site, collection of the samplers after a pre-determined time of exposure to the atmosphere, transportation to the laboratory, elution of the trapped ammonium with deionized water and determination of ammonium by flow injection analysis. This technique permits measurements at low micrograms per cubic meter ($\mu g/m^3$) levels with a time resolution of a few hours.

Badge type passive samplers have also been used for monitoring ambient ammonia concentrations (Rudling et al., 1984; Kasper and Puxbaum, 1994; Rabaud et al., 2001). Badge type samplers normally consist of a plastic cassette housing a 37-mm impregnated (with phosphoric acid, citric acid, sulfuric acid, or oxalic acid) cellulose filter that is used to collect the ammonia. A Teflon prefilter is placed above the impregnated filter to establish a layer of undisturbed air between the filters and to exclude particulate matter. After exposure to the atmosphere for a predetermined length of time, the impregnated filter is removed from the cassette and submerged in water to dissolve the collected ammonia. The solution is then analyzed for ammonia concentrations by a suitable technique (i.e. colorimetry, ion selective electrode, or ion chromatography). These samplers allow ammonia monitoring with a practical detection limit of 0.2 $\mu g/m^3$ for 1 week and 0.05 $\mu g/m^3$ for 4 weeks exposure (Rabaud et al., 2001).

Continuous monitoring

Continuous monitoring has the advantage over time-integrated monitoring of not only being less labour intensive but also of being able to collect measurements over a longer period of time with a much better time resolution and detection limit.

AMANDA - A relatively inexpensive, thoroughly tested and reliable detection system for ammonia is the continuous-flow automated annular denuder (AMANDA) (Wyers et al., 1993; Mennen et al., 1996; Erisman et al., 2001). By automating the denuder technique the precision of the measurement is increased and the risk of contamination is reduced. Furthermore, automation offers the possibility for long-term field measurements. The continuous-flow denuder consists of a rotating annular denuder, a pump, a detector unit and a data logger. Ambient air is drawn through a rotating annular denuder using an airflow rate of 30 L/min. Ammonia is effectively (>99%) absorbed by a weak acid solution covering the walls of the annular space in the rotating denuder.

Two peristaltic pumps, in counterflow with the sampled air, continuously pump the denuder absorption solution in and out at a flow rate of 1.8 milliliters per minute (mL/min). Downstream of the denuder the absorption solution is combined with an alkaline solution in a mixing chamber in a debubbler that results in the formation of gaseous ammonia. The solution then passes a semi-permeable membrane, where approximately 30% of the ammonia diffuses the membrane and is dissolved in a stream of double-demineralized water. The ammonia concentration in the sampled air is calculated from the temperature corrected conductivity and the gas and liquid flows. The data logger registers all data, performs all calculations and stores 1-minute average concentration and temperature values. The detection limit of the continuous-flow annular denuder, defined a three times the standard deviation of zero air measurements (30 minute averages), is 0.07 ppbv (05 $\mu g/m^3$) (Erisman et al., 2001).

Diffusion scrubbing

A more recent innovation for the measurement of atmospheric ammonia is the development of a scrubber (or diffusion scrubber) method. This method combines the attractive features of the annular denuder system with simplicity of operation and the ability to be used for continuous monitoring (Abbas and Tanner, 1981; Frenzel, 1994; Sorensen et al., 1994). The principal of the scrubber system is similar to the annular denuder in which the internal wall of a tube is coated with a suitable substance that acts as a sink for ammonia. The scrubber consists, contrary to the annular denuder, of an outer tube with a water saturated micropourous membrane tube centered along the axis of the tube. The air is sucked through the outer tube at a sufficiently low flow rate (1 – 2 L/min), which insures laminar flow in the tube to prevent turbulence and subsequent deposition of aerosols in the tube.

During passage through the tube, ammonia will diffuse to the liquid membrane tube due to its solubility in water (so the ammonia is collected in the water inside the membrane tube, and not at the walls as in the denuder method). The liquid within the membrane is pumped into a fluorescence system for continuous online measurement of the sampled atmospheric ammonia. Because of the direct flow to the analytical system there is no contamination of the sample due to handling. Therefore, it is possible to achieve a low detection limit of 0.01 ppbv with a sampling resolution time of 10 minutes with this method (Frenzel, 1994). The collection efficiency of ammonia with this method is not 100%. It depends on the length of the membrane, atmospheric pressure, temperature and relative humidity. The materials and simplicity in operating the scrubber system (i.e. no coating, drying, washing, analyzing, and re-coating procedures) make it an affordable and practical method for both laboratory and field studies.

Sniffer method

Another novel detection system suitable for the continuous measurement of atmospheric ammonia levels in the 0.4 to 260-ppbv (0.3 to 180 $\mu g/m^3$) range is the sniffer method (Pranitis and Meyerhoff, 1987). In this system, an appropriate buffer reagent flows through a narrow-bore gas-permeable sniffer tube (either Teflon gas-permeable tubing or Celgard gas-permeable tubing) and on to a flow-through ammonium-selective membrane electrode. The ammonium activity detected by the electrode in the reagent stream is directly proportional to the gas-phase ammonia concentrations surrounding the sniffer tube. Changing the flow rate of the buffer solution and/or the length of the sniffer tube can vary the detection range. This system is simple and selective, relatively mobile, able to sample for long-periods and suitable for field measurements.

Oxidation and chemiluminescence detection

An additional method for the determination of ambient ammonia concentrations and one that is currently employed by Alberta Environment in its mobile air-monitoring laboratory is a continuous measurement instrument based upon the conversion of ammonia to nitrogen oxide with subsequent analysis by chemiluminescence (Breitenbach and Shelef, 1973; Mennen et al., 1996; Alberta Environment, 2001). Chemiluminescence involves mixing an ambient air sample with ozone, which is generated by an internal ozonator. The resulting chemical reaction produces a characteristic light with intensity proportional to the concentration of NO in the sample.

In this method, air is sampled at a flow rate of 0.65 L/min into a chemiluminescence NO_x monitor. A valve routes the air sample into three pathways. In the first path, the air goes directly to the analysis chamber and is reported as the NO concentration. In the second path, the sample passes through a catalytic converter where any NO_2 in the sample is changed to NO. This stream is reported as the concentration of NO_x. The difference of the reported NO_x and NO is the NO_2 concentration. In the third path, the sample passes through a stainless steel N_t converter kept at 850°C on the way to the analysis chamber. Any NH_3 (as well as NO_2) in the sample is changed to NO. The difference of this result (N_t) and the NO_x concentration is reported as the concentration of NH_3. NO, NO_x and NH_3 are measured for 10 seconds each with one measuring cycle lasting 30 seconds. The indirect chemiluminescencent measurement based on the conversion of NH_3 to NO currently lacks sufficient accuracy because of the necessary subtraction of background NO. In addition, the detection limit in the order of 5 $\mu g/m^3$ for ammonia may be inadequate for ambient air monitoring at typical atmospheric concentrations.

Thermodenuders

Thermodenuders are a recently developed alternative to those methods previously mentioned for sampling ammonia in air. These systems rely on high temperature desorption of the ammonia from a metal oxide surface with subsequent or simultaneous catalytic oxidation of ammonia to form the detected species NO. Thermodenuders have the advantage of being less labour intensive, having a short resolution time (10 – 20 minutes), being automated, and being capable of sampling unattended for up to 7 days. Disadvantages include the fact that they may overestimate the ammonia concentrations at very low levels and are relatively expensive.

One reported thermodenuder (Keuken et al., 1989) consists of a V_2O_5-coated annular denuder, a pump, a transportable oven, an NO_x monitor and a data logger. Air is sampled through the annular denuder, where NH3 is adsorbed on the coating with >99% efficiency. After sampling, the oven is heated to 700 °C, then transported over the last 10 cm of the denuder which is heated for five minutes, and after this period transported over the whole denuder which is also heated for five minutes. The adsorbed NH_3 is converted to NO_x and sucked into the NO_x monitor at a flow rate of 60 mL/min using ambient air as a carrier gas. Finally, the oven returns to its initial position for cooling to ambient temperature. A data logger controls the whole system. The NO_x concentration is sampled for both 5-minute periods and integrated by the data logger; the signal measured during the first 10 seconds is used as the baseline calculation. The NH_3 concentration is calculated from the difference between the two integrated peaks, the gas flow and a calibration constant. This thermodenuder has a time resolution of 10 – 20 minutes and a detection limit of 0.1 $\mu g/m^3$ (0.2 ppbv).

Another thermodenuder was developed by KEMA, The Netherlands (Romer et al., 1994) based on the concept of Braman et al. (1982). It consists of two tungsten oxide (WO_3)-coated denuders, a tube supplied with an Aufoil serving as a catalyst, a pump, a NO_x monitor and a computer that controls the instrument and stores data. The denuder and catalyst tubes are wrapped with heating wire. Air is sampled through one of the denuders for 15 minutes. NH_3 and HNO_3 are efficiently (>98%) chemisorbed on the coating. After sampling, the tube is heated to 400°C and flushed with a He/O_2 carrier gas at a flow rate of 100 mL/min, while air is sampled through the other tube, thus providing a continuous measurement. In the heated tube, NH_3 and HNO_3 desorb from the coating and are led through the catalyst, where they are converted to NO at 650 °C. The NO-containing carrier gas is diluted with clean air and drawn into the NO_x monitor at 0.5 L/min. The NO signal is sampled and integrated by the computer in such a way that HNO_3, which desorbs faster than NH_3, is not calculated as NH_3. The sampling time for this system is 10 minutes and the detection limit is 0.04 ppbv.

A final example of a thermodenuder (Langford et al., 1989) is the molybdenum oxide annular denuder system (MOADS). Each denuder consists of an oxidized molybdenum rod supported in a quartz tube (maintained at 50°C) through which air is sampled at a rate of about 1 L/min for a period of 30 minutes. The tube is then heated to 400°C in a flow of nitrogen to desorb the collected NH_3 and any other absorbed species. Part of the collected NH_3 is oxidized to NO in the desorption process and this fraction analyzed using a standard NO-O_3 chemiluminescence detector. Nitric oxide calibration gas is injected into the carrier stream as an internal standard for 4 minutes near the end of each desorption cycle to correct for the drift in the chemiluminescence detector response. The ratio of each NH_3 desorption peak to the corresponding internal standard peak is compared to archived calibration curves to quantify NH_3. Two denuders are used to obtain a continuous record and are mounted in individual compartments that can be separated by as much as 12 meters for gradient measurements. Commercial chromatography software is used for data analysis and the system is fully automated to operate for up to 7 days without user intervention.

Optical methods

Each previously mentioned method uses indirect techniques to measure atmospheric ammonia concentrations through the two-stage process of sample collection and analysis. Direct ammonia measurements by optical techniques based on the spectroscopic properties of the ammonia molecule do not require this two-stage process. Advanced optical methods like DOAS, TDLAS, FTIR, PTD, and PF/LIF have recently been used to directly measure atmospheric concentrations of ammonia. Operationally, these optical methods are capable of accurately following changes in ammonia levels over short time intervals (i.e. 1 minute) with a very low detection limit. With respect to the deployment and operation of these instruments there are some disadvantages: while the systems are automated, they cannot run unattended for long periods of time because the lasers need constant attention; they are very expensive; they are technically complex and use corrosive chemicals; they are fixed monitoring methods; and they require large amounts of electrical power. These instruments, therefore, cannot at present be regarded as being suitable methods for routine measurements in the field.

The use of optical methods to determine ambient ammonia concentrations is demonstrated by the differential optical absorption spectroscopy (DOAS) technique (Gall et al., 1991). The DOAS system is comprised of a light source, a receiver, a detection system and a computer. The light source is a high pressure Xenon lamp generating light in the wavelength region of 200 – 1000 nanometers (nm). A concave mirror collimates the light and the receiver is placed at the other side of the light path. The received light is transmitted by a fibre optic cable to the detection system, consisting of a spectrometer with a rapid scanning device and a computer. Averaged spectra are analyzed by a computer program based on known reference spectra of components absorbing in the measured spectral region. Ammonia concentrations are calculated from the measured and reference spectra.

Another direct spectroscopic technique is the tunable diode laser absorption system (TDLAS) (Cappellani et al., 1985; Mennen et al., 1996). The TDLAS employs a tunable diode laser to scan over a narrow wavelength region for the particular absorption line of ammonia. Ammonia concentrations are determined by monitoring the extent of infrared absorption by the ammonia. The DOAS and TDLAS systems currently lack adequate sensitivity to be of use at concentration levels lower than the few to tens of parts per trillion by volume (pptv) range.

Measurement of ambient ammonia can be carried out using a 25-meter base-path, open multiple reflection optical system coupled to a Fourier Transform Infrared (FTIR) spectrometer (Tuazon et al., 1978). A FTIR system is capable of operating at pathlengths up to 2 kilometers with the use of an eight-mirror multiple reflective cell within the 25 meter base-path. The ammonia concentrations are measured in the same fashion as the other spectroscopic techniques but this method has added high spectral resolution and good time resolution to the strengths of those previous methods. The expense and bulk of this instrument, however, currently makes it an unrealistic choice for the measurement of ammonia concentrations in ambient air.

A recently developed non-intrusive photothermal deflection (PTD) instrument allows sensitive, rapid and quantitative detection of local ammonia concentrations in air (DeVries et al., 1995; Owens et al., 1999). The PDT setup includes a high power waveguide CO_2 pump laser and a deflection unit positioned inside the cavity of the CO_2 laser. Ammonia in the sampled air is vibrationally excited by the infrared CO_2 laser in the intracavity configuration. This heats the immediate area causing a change in refractive index, which is being probed by a second laser beam. This second beam passing over the CO_2 laser beam is deflected by the induced refractive index gradient. The amount of measured deflection is proportional to the concentration of ammonia. The detection limit of this technique for ammonia is 0.5 ppbv and the time resolution is 0.1 seconds. The system is fully automated and suited for non-stop measuring for periods of up to one week. In addition, it is relatively small and simple to operate and it is less expensive, dangerous and requires less power than similar optical techniques.

The photofragmentation/laser-induced fluorescence (PF/LIF) technique has demonstrated to be a highly specific and sensitive method for the quantitative measurement of atmospheric ammonia (Schendel et al., 1990). The PF/LIF technique uses a near-vacuum ultraviolet excimer laser to photolyze the sampled ammonia via a two-photon process, thereby producing a NH photofragment with significant yield in the long-lived metastable electronic state. Within microseconds the prompt luminescence background generated by the photolysis laser will decay by several orders of magnitude. After a short delay time (2 – 10 microsecond) a second probe laser is then used to interrogate the NH state population via excitation of a specific rotationally resolved transition. The resultant fluorescence is then observed in a spectral window that is capable of resolving the vibrational structure of the fluorescing transition. This instrument has the lowest detection limit currently available for ammonia (less than 4 pptv for a 5-minute integration period), is free from interferences, and its performance does not significantly degrade in adverse weather conditions. However, at the present time the cost and bulk of the equipment and the need for highly trained operators limits its widespread use.

APPENDIX C

REVIEW OF AIR QUALITY GUIDELINES FOR AMMONIA USED BY AGENCIES IN NORTH AMERICA AND ELSEWHERE

Agency:

Ontario Ministry of the Environment (OME).

Ammonia Air Quality Guideline:

Ambient air quality criterion (AAQC) = 100 µg/m^3 (recommended).

Averaging Time To Which Guideline Applies:

24-hour averaging time.

Basis for Development:

Based on the US Environmental Protection Agency reference concentration (RfC).

Date Guideline Developed:

March 2001.

How Guideline is Used in Practice:

Used by Ontario Ministry of Environment (OME) to represent human health or environmental effect-based values not expected to cause adverse effects based on continuous exposure.

Additional Comments:

AAQC is not used by OME to permit stationary sources that emit ammonia to the atmosphere.

Reference and Supporting Documentation:

Ontario Ministry of the Environment (Ontario MOE). 2001. *Ontario Air Standards for Ammonia*. Standards Development Branch, Ontario Ministry of the Environment. Toronto, ON. March 2001. 52 pp.

Agency:

Ontario Ministry of the Environment (OME).

Ammonia Air Quality Guideline:

Maximum point of impingement (POI) = 3,600 $\mu g/m^3$.

Averaging Time To Which Guideline Applies:

30-minute averaging time.

Basis for Development:

Based on odour considerations [no other supporting data available].

Date Guideline Developed:

1985.

How Guideline is Used in Practice:

Used by OME to review permit applications for stationary sources that emit ammonia to the atmosphere.

Additional Comments:

n/a

Reference and Supporting Documentation:

Ontario Ministry of the Environment (Ontario MOE). 2001. *Ontario Air Standards for Ammonia*. Standards Development Branch, Ontario Ministry of the Environment. Toronto, ON. March 2001. 52 pp.

Agency:

US Agency for Toxic Substances and Disease Registry (ATSDR).

Ammonia Air Quality Guideline:

Chronic inhalation minimum risk level (MRL) = 0.3 ppm (208 $\mu g/m^3$).

Averaging Time To Which Guideline Applies:

365 days and longer (i.e. continuous exposure over a lifetime).

Basis for Development:

Absence of respiratory irritation in man. The NOAEL from a single human occupational 15-week study of chronic-duration inhalation exposure was used to derive the chronic inhalation MRL. After adjusting for intermittent exposure, the NOAEL was divided by a safety factor of 10 for human variability.

Date Guideline Developed:

December 1990.

How Guideline is Used in Practice:

MRLs are intended to serve as a screening tool to help public health professionals decide where to look more closely. Inhalation MRLs are exposure concentrations that, based on current information, might cause adverse health effects in the people most sensitive to such substance-induced effects for 365 days, and longer, exposure durations.

Additional Comments:

Inhalation MRLs provide a basis for comparison with levels that people might encounter in air. If a person is exposed to ammonia at an amount below the MRL, it is not expected that harmful (noncancer) health effects will occur. Because these levels are based only on information currently available, some uncertainty is always associated with them. Also, because the method for deriving MRLs does not use any information about cancer, an MRL does not imply anything about the presence, absence, or level of risk for cancer.

Reference and Supporting Documentation:

Agency for Toxic Substances and Disease Registry (ATSDR). 1990. *Toxicological Profile for Ammonia.* ATSDR, Public Health Service, US Department of Health and Human Services. Atlanta, GA. December 1990. 137 pp.

Agency:

US Environmental Protection Agency (EPA).

Ammonia Air Quality Guideline:

Reference concentration (RfC) = 100 $\mu g/m^3$.

Averaging Time To Which Guideline Applies:

Continuous exposure (daily exposure over a lifetime).

Basis for Development:

Based on decreased pulmonary function and changes in subjective syptomatology of production workers exposed via inhalation to ammonia in a soda ash facility (8-hour TWA occupational exposure). A human equivalent concentration (HEC) LOAEL of 2.3 mg/m^3 was adjusted with a total uncertainty factor of 30, and after rounding to one significant digit, a value of 100 $\mu g/m^3$ was derived.

Date Guideline Developed:

Last revised in 1991.

How Guideline is Used in Practice:

The Reference concentration (RfC) is intended for use by US EPA staff in risk assessments, decision-making and regulatory activities.

Additional Comments:

The Integrated Risk Information System (IRIS) is prepared and maintained by the US EPA. IRIS is an electronic database containing information on human health effects that may result from exposure to various chemicals in the environment.

Reference and Supporting Documentation:

US Environmental Protection Agency. *Integrated Risk Information System*. http://www.epa.gov/iris/ (accessed 8 August 2001).

Agency:

California Environmental Protection Agency (Cal EPA).

Ammonia Air Quality Guideline:

Acute reference exposure level (REL) = 3,200 µg/m^3.

Averaging Time To Which Guideline Applies:

1-hour averaging time.

Basis for Development:

Eye and respiratory irritation in exposed humans. Exposure concentrations to humans from four studies were adjusted to 1-hour durations using a "toxic load" formula ($C^n \times T = K$). The acute REL was calculated by a benchmark concentration (BC) approach using a log-normal probit analysis of data from the four studies and applying an uncertainty factor (UF) of 3 to account for intraspecies variation in the human population.

Date Guideline Developed:

March 1999.

How Guideline is Used in Practice:

Acute RELs are for use in facility health risk assessments conducted for the AB 2588 Air Toxics "Hot Spots" Program.

Additional Comments:

n/a

Reference and Supporting Documentation:

California Environmental Protection Agency (Cal EPA). 1999. *Determination of Acute Reference Exposure Levels for Airborne Toxicants*. Office of Environmental Health Hazard Assessment, Air Toxicology and Epidemiology Section, California Environmental Protection Agency. Oakland, CA. March 1999.

Agency:

California Environmental Protection Agency (Cal EPA).

Ammonia Air Quality Guideline:

Chronic reference exposure level (REL) = 200 $\mu g/m^3$.

Averaging Time To Which Guideline Applies:

Continuous exposure (daily exposure over a lifetime).

Basis for Development:

Protection against respiratory irritation [no other supporting data available].

Date Guideline Developed:

February 2000.

How Guideline is Used in Practice:

Acute RELs are for use in facility health risk assessments conducted for the AB 2588 Air Toxics "Hot Spots" Program.

Additional Comments:

n/a

Reference and Supporting Documentation:

California Environmental Protection Agency (Cal EPA). 2000. *Air Toxics Hot Spots Program Risk Assessment Guidelines Part III. Technical Support Document for the Determination of Noncancer Chronic Reference Exposure Levels.* Office of Environmental Health Hazard Assessment, Air Toxicology and Epidemiology Section, California Environmental Protection Agency. Oakland, CA. February 2000.

California Air Pollution Control Officers Association (CAPCOA). 1993. *Air Toxics Hot Spots Program Revised 1992 Risk Assessment Guidelines.* CAPCOA Toxics Committee, Cameron Park, CA. October 1993.

Agency:

Louisiana Department of Environmental Quality (DEQ).

Ammonia Air Quality Guideline:

Ambient air standard (AAS) for toxic air pollutants = 640 μg/m^3.

Averaging Time To Which Guideline Applies:

8-hour averaging time.

Basis for Development:

Not stated.

Date Guideline Developed:

Not stated.

How Guideline is Used in Practice:

Used by Louisiana DEQ to review permit applications for stationary sources that emit ammonia to the atmosphere.

Additional Comments:

Not applicable to emissions from soil or foliar application of ammonia in agricultural practices.

Reference and Supporting Documentation:

Louisiana Administrative Code (LAC). Title 33 Environmental Quality, Part III Air, Chapter 51. Louisiana Department of Environmental Quality. Baton Rouge, LA.

Agency:

Michigan Department of Environmental Quality (DEQ).

Ammonia Air Quality Guideline:

Initial threshold screening level (ITSL) = 100 $\mu g/m^3$.

Averaging Time To Which Guideline Applies:

24-hour averaging time.

Basis for Development:

Developed after US EPA Reference Concentration (based on decreased pulmonary function and changes in subjective syptomatology of production workers exposed via inhalation to ammonia in a soda ash facility (8-hour TWA occupational exposure)).

Date Guideline Developed:

1991.

How Guideline is Used in Practice:

Application of the ITSL is required for any new or modified emission source or sources for which a permit to install is requested and which emits a toxic air contaminant. There are two basic requirements of Michigan air toxic rules. First, each source must apply the best available control technology for toxics (T-BACT). After the application of T-BACT, the emissions of the toxic air contaminant cannot result in a maximum ambient concentration that exceeds an applicable health based screening level (ITSL).

Additional Comments:

n/a

Reference and Supporting Documentation:

Michigan Administrative Code (MAC). Air Pollution Control Rules. Part 2 Air Use Approval, R 336.1201 - 336.1299. Air Quality Division, Department of Environmental Quality. Lansing, MI.

Agency:

New Hampshire Department of Environmental Services (DES).

Ammonia Air Quality Guideline:

24-hour ambient air limit (AAL) = 100 µg/m^3.
Annual ambient air limit (AAL) = 100 µg/m^3.

Averaging Time To Which Guideline Applies:

See above.

Basis for Development:

In the case of ammonia, the AALs were developed in the following manner:

24-hour Ambient Air Limit – The American Conference of Governmental Industrial Hygienists (ACGIH) 8-hour time weighted average occupational exposure limit (OEL) of 17 mg/m^3 is divided by a safety factor (SF) of 71 and a time adjustment factor (TAF) of 2.5.

Annual Ambient Air Limit – The reference concentration (RfC) limit established by the US Environmental Protection Agency is used as the annual AAL.

Date Guideline Developed:

May 1998.

How Guideline is Used in Practice:

Used by New Hampshire DES to review permit applications for sources that emit ammonia to the atmosphere. Sources are regulated through a statewide air permitting system and include any new, modified or existing stationary source, area source or device.

Additional Comments:

n/a

Reference and Supporting Documentation:

New Hampshire Administrative Rule. Chapter Env-A 1400. Regulated Toxic Air Pollutants. New Hampshire Department of Environmental Services. Concord, NH.

Agency:

New Jersey Department of Environmental Protection (DEP).

Ammonia Air Quality Guideline:

Applicants are required to carry out a risk assessment in conjunction with applying for an air pollution control pre-construction permit. In the case of ammonia, the US EPA RfC (100 $\mu g/m^3$) is used as the pollutant-specific reference concentration in which to calculate a Hazard Quotient for sources that emit ammonia to the atmosphere.

Averaging Time To Which Guideline Applies:

Continuous exposure (daily exposure over a lifetime).

Basis for Development:

Developed after US EPA Reference Concentration (based on decreased pulmonary function and changes in subjective syptomatology of production workers exposed via inhalation to ammonia in a soda ash facility (8-hour TWA occupational exposure)).

Date Guideline Developed:

December 1994.

How Guideline is Used in Practice:

Used by New Jersey DEP to review permit applications for sources that emit ammonia to the atmosphere.

Additional Comments:

n/a

Reference and Supporting Documentation:

New Jersey Administrative Code (NJAC). Title 7, Chapter 27, Subchapter 8. Permits and Certificates for Minor Facilities (and Major Facilities without an Operating Permit). New Jersey Department of Environmental Protection. Trenton, NJ.

New Jersey Department of Environmental Protection. 1994. *Technical Manual 1003. Guidance on Preparing a Risk Assessment for Air Contaminant Emissions.* Air Quality Permitting Program, Bureau of Air Quality Evaluation, New Jersey Department of Environmental Protection. Trenton, NJ. Revised December 1994.

Agency:

North Carolina Department of Environment and Natural Resources (ENR).

Ammonia Air Quality Guideline:

Acceptable ambient level (AAL) = 2,700 $\mu g/m^3$.

Averaging Time To Which Guideline Applies:

1-hour averaging time.

Basis for Development:

Not stated.

Date Guideline Developed:

1990.

How Guideline is Used in Practice:

A facility emitting ammonia must limit its emissions so that the resulting modeled ambient levels at the property boundary remain below the health-based acceptable ambient level (AAL).

Additional Comments:

n/a

Reference and Supporting Documentation:

North Carolina Administrative Code (NCAC). North Carolina Air Quality Rules 15A NCAC 2D.1100 – Air Pollution Control Requirements (Control of Toxic Air Pollutants). North Carolina Department of Environment and Natural Resources. Raleigh, NC.

North Carolina Administrative Code (NCAC). North Carolina Air Quality Rules 15A NCAC 2Q.0700 – Air Quality Permit Procedures (Toxic Air Pollutant Procedures). North Carolina Department of Environment and Natural Resources. Raleigh, NC.

Agency:

Ohio Environmental Protection Agency (EPA).

Ammonia Air Quality Guideline:

Maximum acceptable ground-level concentration (MAGLC) = 170 $\mu g/m^3$ (proposed).

Averaging Time To Which Guideline Applies:

1-hour averaging time.

Basis for Development:

$$\text{MAGCL} = \frac{\text{TLV}}{10} \times \frac{8\ \text{hr}}{24\ \text{hr}} \times \frac{5\ \text{d}}{7\ \text{d}} \times \frac{30\ \text{yr}}{70\ \text{yr}} = \frac{\text{TLV}}{100}.$$

The TLV is the American Conference of Governmental Industrial Hygienist (ACGIH) 8-hour time weighted average occupational exposure limit (OEL) of 17 mg/m^3. The TLV is adjusted by a safety factor of 10 to take into account greater susceptibility of the general population in comparison to healthy workers. The 8/24 and the 5/7 multipliers are used to relate the exposure to longer than 40-hour time periods and ascertain that the individual's total exposure will be no greater than that allowed by the TLV. The 30/70 multiplier is used to relate the difference in exposure duration from a possible working lifetime of 30 years to the average life exposure assumption of 70 years.

Date Guideline Developed:

January 1994 (proposed).

How Guideline is Used in Practice:

Used by Ohio EPA to review permit applications for sources that emit ammonia to the atmosphere.

Additional Comments:

n/a

Reference and Supporting Documentation:

Ohio Environmental Protection Agency (Ohio EPA). 1994. *Review of New Sources of Air Toxic Emissions. Proposed for Public Comment.* Division of Air Pollution Control, Ohio EPA. Columbus, OH. January 1994. 31 pp.

Agency:

Oklahoma Department of Environmental Quality (DEQ).

Ammonia Air Quality Guideline:

Maximum acceptable ambient concentration (MAAC) = 1,742 $\mu g/m^3$ (anhydrous ammonia).

Averaging Time To Which Guideline Applies:

24-hour averaging time.

Basis for Development:

The American Conference of Governmental Industrial Hygienist (ACGIH) TLV – 8-hour time weighted average occupational exposure limit (OEL) of 17 mg/m^3 – is divided by a safety factor of 10 for substances of low toxicity, such as ammonia.

Date Guideline Developed:

Not stated.

How Guideline is Used in Practice:

Used by Oklahoma DEQ to review permit applications for sources that emit ammonia to the atmosphere.

Additional Comments:

n/a

Reference and Supporting Documentation:

Oklahoma Administrative Code (OAC). Title 252. Chapter 100. Air Pollution Control. 100:252-41 - Control of Emission of Hazardous and Toxic Air Contaminants. Oklahoma Department of Environmental Quality. Oklahoma City, OK.

Agency:

Rhode Island Department of Environmental Management (DEM).

Ammonia Air Quality Guideline:

No guideline exists for ammonia.

Averaging Time To Which Guideline Applies:

n/a

Basis for Development:

n/a

Date Guideline Developed:

n/a

How Guideline is Used in Practice:

n/a

Additional Comments:

n/a

Reference and Supporting Documentation:

Rhode Island Department of Environmental Management. 1992. Air Pollution Control Regulation No. 22. Division of Air and Hazardous Materials, Rhode Island Department of Environmental Management. Providence, RI. Amended 19 November 1992.

Agency:

Texas Natural Resource Conservation Commission (TRNCC).

Ammonia Air Quality Guideline:

Short-term effects screening level (ESL) = 170 $\mu g/m^3$.
Long-term effects screening level (ESL) = 17 $\mu g/m^3$.

Averaging Time To Which Guideline Applies:

1-hour averaging time for short-term ESL.
Annual averaging time for long-term ESL.

Basis for Development:

Short-term Effects Screening Level – The American Conference of Governmental Industrial Hygienist (ACGIH) TLV – 8-hour time weighted average occupational exposure limit (OEL) of 17 mg/m^3 – is divided by a safety factor of 100.

Long-term Effects Screening Level – The ACGIH TLV – 8-hour time weighted average occupational exposure limit (OEL) of 17 mg/m^3 – is divided by a safety factor of 1000.

Date Guideline Developed:

Not stated.

How Guideline is Used in Practice:

ESLs are used to evaluate the potential for effects to occur as a result of exposure to concentrations of constituents in air. ESLs are based on data concerning health effects, odor nuisance potential, effects with respect to vegetation, and corrosion effects. They are not ambient air standards. If predicted or measured airborne levels of a chemical do not exceed the screening level, adverse health or welfare effects would not be expected to result. If ambient levels of constituents in air exceed the screening levels, it does not necessarily indicate a problem, but rather, triggers a more in-depth review.

Additional Comments:

n/a

Reference and Supporting Documentation:

Texas Natural Resource Conservation Commission (TNRCC) 2001. *Toxicology & Risk Assessment (TARA) Section Effects Screening Levels*. http://www.tnrcc.state.tx.us/permitting/tox/index.html (accessed 6 September 2001).

Agency:

Vermont Agency of Natural Resources.

Ammonia Air Quality Guideline:

Hazardous ambient air standard (HAAS) = 1,800 $\mu g/m^3$.

Averaging Time To Which Guideline Applies:

8-hour averaging time.

Basis for Development:

Irritant (respiratory) health effects. The HAAS for a chemical which causes either chronic or irritant health effects is set at the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV) divided by an uncertainty factor and an accumulation factor. In the case of ammonia, the uncertainty factor was 10 based on using toxicological data from valid experimental results of studies on prolonged ingestion by man with no indication of carcinogenicity and the accumulation factor was 4.2

Date Guideline Developed:

Not stated.

How Guideline is Used in Practice:

Used by Vermont ANR to review permit applications for stationary sources that emit ammonia to the atmosphere.

Additional Comments:

n/a

Reference and Supporting Documentation:

Vermont Air Pollution Control Regulations. 2001. State of Vermont Agency of Natural Resources. Air Pollution Control Division. Waterbury, VT. 29 November 2001. 187 pp.

Agency:

Washington State Department of Ecology (DOE).

Ammonia Air Quality Guideline:

Acceptable source impact level (ASIL) = 100 µg/m³.

Averaging Time To Which Guideline Applies:

24-hour averaging time.

Basis for Development:

The Reference Concentration (RfC) limit established by the US Environmental Protection Agency is used as the 24-hour ASIL.

Date Guideline Developed:

September 1991.

How Guideline is Used in Practice:

Used by Washington State DOE to review permit applications for sources that emit ammonia to the atmosphere.

Additional Comments:

n/a

Reference and Supporting Documentation:

Washington Administrative Code (WAC). Chapter 173-460 WAC. Controls For New Sources Of Toxic Air Pollutants. Washington State Department of Ecology. Olympia, WA.

Agency:

Wisconsin Department of Natural Resources (DNR).

Ammonia Air Quality Guideline:

Ambient air concentration (AAC) = 432 $\mu g/m^3$.

Averaging Time To Which Guideline Applies:

24-hour averaging time.

Basis for Development:

Two and four-tenths percent of the American Conference of Governmental Industrial Hygienist (ACGIH) TLV – 8-hour time weighted average occupational exposure limit (OEL) of 17 mg/m^3 – is used to derive the 24-hour AAC for ammonia. This is equivalent to TLV/42.

Date Guideline Developed:

Not stated.

How Guideline is Used in Practice:

Used by Wisconsin DNR to review permit applications for sources that emit ammonia to the atmosphere.

Additional Comments:

n/a

Reference and Supporting Documentation:

Wisconsin Administrative Code (WAC). Air Pollution Control Rules. Chapter NR 445. Control of Hazardous Pollutants. Wisconsin Department of Natural Resources. Madison WI.

Agency:

New Zealand Ministry for the Environment and New Zealand Ministry of Health.

Ammonia Air Quality Guideline:

Ambient air quality guidelines are proposed for selected air toxics, however ammonia is not included.

Averaging Time To Which Guideline Applies:

n/a

Basis for Development:

n/a

Date Guideline Developed:

n/a

How Guideline is Used in Practice:

n/a

Additional Comments:

n/a

Reference and Supporting Documentation:

New Zealand Ministry for the Environment and Ministry of Health (New Zealand). 2000. *Proposals for Revised and New Ambient Air Quality Guidelines. Discussion Document.* Air Quality Technical Report No 16. Prepared by the Ministry for the Environment and the Ministry of Health. December 2000. 86 pp.

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ASSESSMENT REPORT ON

AMMONIA

FOR DEVELOPING AMBIENT AIR QUALITY OBJECTIVES

- *VOLUME II* – *Vegetation Effects*

Alberta
Environment

ASSESSMENT REPORT ON
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FOR DEVELOPING AMBIENT AIR QUALITY OBJECTIVES

VOLUME II – VEGETATION EFFECTS

Prepared for
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by
Dr. Sagar Krupa

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FOREWORD

Alberta Environment maintains Ambient Air Quality Objectives to support air quality management in Alberta. Alberta Environment currently has ambient objectives for thirty-one substances and five related parameters. These objectives are periodically updated and new objectives are developed as required. Fact Sheets on Ambient Air Quality Guidelines were updated in September 1997 and February 2000.

With the assistance of the Clean Air Strategic Alliance, a multi-stakeholder workshop was held in October 2000 to set Alberta's priorities for the next three years. Based on those recommendations, a three-year work plan ending March 31, 2004 was developed to review four existing guidelines, create three new guidelines for three families of substances, and adopt six new guidelines from other jurisdictions.

This document is one in a series of documents that presents the scientific assessment for these substances.

Ahmed Idriss, Ph.D., P.Eng.
Project Manager
Science and Standards Branch

NOTE: The *Environmental Protection and Enhancement Act*, Part 1, Section 14(1) refers to "ambient environmental quality objectives" and uses the term "guidelines" in Section 14(4) to refer to "procedures, practices and methods for monitoring, analysis and predictive assessment." For consistency with the Act, the historical term "ambient air quality guidelines" is being replaced by the term "ambient air quality objectives." This document was prepared as the change in usage was taking place. Consequently any occurrences of "air quality guideline" in an Alberta context should be read as "air quality objective."

ACKNOWLEDGEMENTS

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Note to the reader: The first two sections in this supplemental report provide only a brief overview, as a preamble to the descriptions of the effects of NH_3 on terrestrial vegetation. For additional information on the topics described in these two sections, the reader is referred to the relevant portions of Volume I of the report, submitted by WBK & Associates Inc. entitled "Assessment Report on Ammonia for Developing Ambient Air Quality Objectives".

TABLE OF CONTENTS

FOREWORD ..... **i**
ACKNOWLEDGEMENTS ..... **ii**
LIST OF TABLES ..... **v**
LIST OF FIGURES ..... **vi**
SUMMARY ..... **vii**

1.0 INTRODUCTION **1**

2.0 ATMOSPHERIC CHEMISTRY, TRANSPORT, CONCENTRATIONS AND DEPOSITION OF AMMONIA (NH_3) AND AMMONIUM (NH_4^+) ON TO VEGETATION AND SOILS **2**
- 2.1 Chemistry 2
- 2.2 Transport 2
- 2.3 Concentrations 3
- 2.4 Deposition 4

3.0 EFFECTS OF NH_3 AND NH_4^+ (NH_Y) ON VEGETATION **6**
- 3.1 Uptake of NH_y by Shoots and by Roots 6
  - *3.1.1 NH_3 (shoots)* *6*
  - *3.1.2 NH_4^+ (shoots)* *8*
  - *3.1.3 NH_y (roots)* *8*
- 3.2 Assimilation and Detoxification of NH_Y 9
- 3.3 Metabolic Changes Due to NH_Y Assimilation and Detoxification 10
- 3.4 Changes in Leaf Gas Exchange Following Exposure to NH_y 11
  - *3.4.1 Effects of NH_y onEepicuticular Waxes* *12*
  - *3.4.2 Factors Determining the Toxicity of NH_y* *12*
- 3.5 Direct Toxicity of NH_y and Visible Foliar Injury 14

4.0 SECONDARY EFFECTS OF NH_Y UPTAKE AND ASSIMILATION ON VEGETATION **18**
- 4.1 Growth Responses 18
- 4.2 Resistance to Stress 19
  - *4.2.1 Drought Resistance* *19*
  - *4.2.2 Frost Resistance* *19*
  - *4.2.3 Insect Pests* *19*
  - *4.2.4 Pathogens* *20*
- 4.3 Mycorrhizae 20

5.0 INTERACTIVE OR JOINT EFFECTS OF NH_Y WITH OTHER AIR POLLUTANTS ON VEGETATION 22

6.0 EFFECTS OF N DEPOSITION AT THE ECOSYSTEM LEVEL 23
- 6.1 Soil Processes 23
  - *6.1.1 N Saturation* 23
  - *6.1.2 Acidification* 25
- 6.2 Ecosystem Responses 25
  - *6.2.1 Effects on Heathlands* 25
  - *6.2.2 Effects on Species-rich Grasslands* 26
  - *6.2.3 Effects on Forests* 27

7.0 EFFECTS OF N DEPOSITION ON EPIPHYTIC LICHENS AND GREEN ALGAE 29
- 7.1 Lichens 29
- 7.2 Green Algae 30

8.0 AIR QUALITY INDICATORS FOR PROTECTING VEGETATION 31
- 8.1 Critical Levels 31
- 8.2 Critical Loads 31
  - *8.2.1 Critical Levels (NH_3)* 31
  - *8.2.2 Critical Loads (N)* 32

9.0 CONCLUSIONS 34

10.0 REFERENCES 36

LIST OF TABLES

Table 1 Deposition velocities (V_d) for NH_3 and NH_4^+ (cm s^{-1}) 60

Table 2 NH_4^+-N deposition (kg N ha^{-1} yr^{-1}) in open field and under different plant canopies 61

Table 3 Summary of effects of NH_3 exposures on plants 62

Table 4 Relative susceptibilities of plant species to acute ammonia injury, based on estimated percentage of foliar injury of ten or more plants observed in two or more episodes. Xs represent estimation of variability of response to ammonia as observed in the field or based on results of artificial exposure experiments [a] 77

Table 5 Nitrogen saturated forests in North America including estimated N inputs and outputs 81

Table 6 Importance of environmental variables with a significant ($P \leq 0.05$) effect on lichen vegetation 83

Table 7 Fundamental differences in the effects of atmospheric SO_2 and NH_3 on terrestrial higher plants and epiphytic lichens [a] 84

Table 8 Critical levels for NH_3 85

Table 9 Critical loads for N 86

LIST OF FIGURES

Figure 1 Pathways and factors governing the effects of NH_3 on plants. Source: modified from Fangmeier et al. (1994) 7

Figure 2 Glutamine synthetase (GS) - Glutamate synthase (GOGAT) pathway of NH_3 assimilation in plants 9

Figure 3 (A). Row of table beet (Beta vulgaris) exposed to acute (relatively high) anhydrous NH_3 concentrations due to an industrial malfunction. (B). Close-up of a table beet leaf showing acute response to anhydrous NH_3. Note the death of the leaf tissue (brown areas) between the veins. These symptoms are very similar to those induced by acute exposure to SO_2 16

Figure 4 (A) Cherry tomato (Lycopersicon esculentum var. cerasiforme) showing acute response (white bleached areas between the veins) to anhydrous NH_3. (B). Epiphytic lichens on the trunk of an oak tree exhibiting purple colouration due to acute exposure to anhydrous NH_3. This response can be used as a biological indicator of NH_3 pollution 17

Figure 5 The nitrogen cycle, emphasizing the primary biological transformations (large shaded circle) the means of replenishment and the losses from the soil. Chemical fertilizers from industrial nitrogen fixation are an increasingly important source of this element, but excessive use has serious environmental implications. D/W = Respectively, dry and wet atmospheric deposition. Source: modified from Brady (1990) 24

Figure 6 Modeled relationships between the maximum NH_3 emissions, with no exceedances of the 'no observable effect level' and distance between the source and a sensitive receptor. Area above the upper curve indicates that the emissions are too high or the source is at a too short a distance from the sensitive receptor. The lower curve indicates situations where the prevailing wind direction is from the source to the sensitive receptor. While the lower curve reflects high background NH_3 concentrations, the upper curve reflects the opposite. Source: Van der Eerden et al. (1998) 33

SUMMARY

At the global scale, among all N (nitrogen) species in the atmosphere and their deposition on to terrestrial vegetation and other receptors, NH_3 (ammonia) is considered to be the foremost. The major sources for atmospheric NH_3 are agricultural activities and animal feedlot operations, followed by biomass burning (including forest fires) and to a lesser extent fossil fuel combustion. Close to its sources, acute exposures to NH_3 can result in visible foliar injury on vegetation. NH_3 is deposited rapidly within the first 4-5 km from its sources. However, NH_3 is also converted in the atmosphere to fine particle NH_4^+ (ammonium) aerosols that are a regional scale problem.

Much of our current knowledge of the effects of NH_3 on higher plants is predominantly derived from the studies conducted in The Netherlands, although there are many published reports from other parts of Europe. Adverse effects on vegetation occur when the rate of foliar uptake of NH_3 is greater than the rate and capacity for in vivo detoxification by the plants. Most to least sensitive plant species to NH_3 are native vegetation > forests > agricultural crops. There are also a number of studies on N deposition and lichens, mosses and green algae. Direct cause and effect relationships in those cases are confounded by other environmental factors, particularly changes in the ambient SO_2 (sulphur dioxide) concentrations.

In addition to the direct foliar injury, adverse effects of NH_3 on higher plants include alterations in: growth and productivity, tissue content of nutrients and toxic elements, drought and frost tolerance, responses to insect pests and disease causing microorganisms (pathogens), development of beneficial root symbiotic or mycorrhizal associations and inter species competition or bio-diversity. In all these cases, the joint effects of NH_3 with other air pollutants such as the all-pervasive O_3 or the increasing CO_2 concentrations are poorly understood.

While NH_3 uptake in higher plants occurs through the shoots, NH_4^+ uptake occurs through the shoots, roots and through both pathways. However, NH_4^+ is immobile in the soil and is converted to NO_3^- (nitrate). In agricultural systems, additions of NO_3^- to the soil (initially as NH_3 or NH_4^+) and the consequent increases in the emissions of N_2O (nitrous oxide, a greenhouse gas) and leaching of NO_3^- into the ground and surface waters are of major environmental concern.

At the ecosystem level NH_3 deposition cannot be viewed alone, but in the context of total N deposition. There are a number of forest ecosystems in North America (including Canada) that have been subjected to N saturation and the consequent negative effects. Regulatory mitigative approaches to these problems include the use of N saturation data or the concept of critical loads. Current information suggests that a critical load of 5-10 kg ha^{-1} yr^{-1} of total N deposition (both dry and wet deposition combined of all atmospheric N species) would protect the most vulnerable terrestrial ecosystems (heaths, bogs, cryptogams) and values of 10-20 kg ha^{-1} yr^{-1} would protect forests, depending on their soil conditions. However, to derive the best analysis, the critical load concept should be coupled to the results and consequences of N saturation.

1.0 INTRODUCTION

Naturally occurring nitrogen (N_2) constitutes 78% of the dry troposphere (up to 10-15 km above the earth's surface). However, additions of anthropogenic (human-made) nitrogen (N) compounds constitute one of the four major classes of air pollutants of significance to human health and the environment. The other three classes are sulphur compounds, volatile and semi-volatile organic compounds and toxic metals (Finlayson-Pitts and Pitts, 1999). Atmospheric N species occur as gases, vapours (hydrated gas molecules) and particles (both solid and liquid). These are oxides of nitrogen (NO_x, composed of nitric oxide, NO and nitrogen dioxide, NO_2), ammonia (NH_3) and nitrous oxide (N_2O), peroxy acyl nitrates (peroxy acetyl nitrate or PAN being the most studied among them), nitric acid (HNO_3), ammonium (NH_4^+) and other inorganic and organic nitrates (NO_3^-s).

Among the atmospheric N species, NH_3 is emitted by a large number of sources such as volatilization from animal waste and synthetic fertilizers, biomass burning (including forest fires), losses from soils under native vegetation and agricultural crops, emissions from human excreta and fossil fuel combustion (Olivier et al., 1996; Lee et al., 1997; Bouwman et al., 1997).

Total anthropogenic emissions of NH_3, NO_x and N_2O respectively account for 43.0 (36%), 31.1 (26%) and 3.2 (approx. 3%) million tons of N annually to the total global budget that includes natural sources (Olivier et al., 1998). Of the total anthropogenic emissions, NH_3 accounts for 55%, NO_x for 40% and N_2O for about 5%. With regard to total N (all three species combined) emissions, agriculture is by far the largest source (about 50%) and stationary and mobile source fossil fuel combustion each contributes 15%, whereas biomass burning contributes another 10%.

It was estimated that during 1990, China emitted 8,449 Gg NH_3-N yr^{-1} (1 Gg = 10^9 g). In contrast estimates for USA and Canada were respectively 2,898 and 456 Gg (Olivier et al., 1998).

2.0 ATMOSPHERIC CHEMISTRY, TRANSPORT, CONCENTRATIONS AND DEPOSITION OF AMMONIA (NH_3) AND AMMONIUM (NH_4^+) ON TO VEGETATION AND SOILS

2.1 Chemistry

NH_3 is a very important basic compound in the atmosphere. It reacts readily with acidic substances such as sulfuric acid (H_2SO_4), nitric acid (HNO_3), nitrous acid (HNO_2), or hydrochloric acid (HCl) to form ammonium salts that occur predominantly in the fine particle (size < 2.5 μm) fraction (Finlayson-Pitts and Pitts, 1999). A small amount of NH_3 (approximately 1%) reacts with hydroxy (OH) radicals to form $NH_2 + H_2O$, which is subsequently oxidized to NO by HNO_3 (Galbally and Roy, 1983).

The formation of fine particulate NH_4^+ salts is a very effective mechanism in removing gaseous NH_3 from the atmosphere. Estimates of the conversion rates of NH_3 to NH_4^+ vary between $10^{-3}\ s^{-1}$ (Vermetten et al., 1985) and $5 \times 10^{-5}\ s^{-1}$ (Erisman et al., 1988). This conversion is most effective in the lowest (100 m) layer of the atmosphere above the surface (Lenhard and Gravenhorst, 1980) and is much faster during the daytime than at night (Erisman et al., 1988).

2.2 Transport

Since NH_3 is either readily converted to NH_4^+ or subjected to dry deposition, high concentrations are found only close to the surface and near to emission sources. With discrete or isolated NH_3 sources, concentrations decrease significantly within the lower 200 m of the atmosphere (Vermetten et al., 1985; Erisman et al., 1987) and can reach background levels at 1500 m in the winter and 3000 m in the summer (Georgii and Müller, 1974; Georgii and Lenhard, 1978; Lenhard and Gravenhorst, 1980; Levine et al., 1980; Alkezweeny et al., 1986). Horizontal concentration profiles show a clear decrease with increasing distance from the source (50% reduction at 600 m from the source (Erisman et al., 1987) and 70% decrease at 4 km (Asman et al., 1989). Different estimates have been reported for the residence time of NH_3 ranging from 2.8 h during the daytime and 5 h at night (Erisman et al., 1988), 0.8 days (Möller and Schieferdecker, 1985), 1-4 days (Söderlund and Svensson, 1976) and 4 days (Dawson, 1984).

In the atmosphere, laws of gravity do not readily influence fine particle deposition on to surfaces. They are transferred on to surfaces by Brownian motion and thus ammonium sulfate [$(NH_4)_2SO_4$] and ammonium nitrate [NH_4NO_3] have low deposition velocities and prolonged atmospheric residence times. Assuming an atmospheric residence time of 6 days and a wind velocity of $5\ m\ s^{-1}$, the transport distance of $(NH_4)_2\ SO_4$ and NH_4NO_3 may be as large as 2,500 km (Irwin and Williams, 1988).

Vertical profiles of NH_4^+ concentrations are far less pronounced than NH_3. In contrast to NH_3 (high concentrations close to the surface), NH_4^+ concentrations were found to be higher than NH_3 at heights above 200 m (Georgii and Lenhard, 1978; Lenhard and Gravenhorst, 1980; Vermetten et al., 1985; Erisman et al., 1987, 1988). Horizontal profiles of NH_4^+ were also rather homogeneous (Allen et al., 1988; Janssen et al., 1989) with only relatively small increases near NH_3 sources (Vermetten et al., 1985). Estimates of the residence time of NH_4^+ were 4-7 days

(Bonis et al., 1980), 7.7 days (Möller and Schieferdecker, 1985), 7-19 days (Söderlund and Svensson, 1976) and 15 ± 9 days (Böttger et al., 1978).

2.3 Concentrations

Atmospheric NH_3 concentrations are not routinely measured by governmental air quality monitoring networks. This has led to significant uncertainities in the calculations of total dry deposition of N (Krupa and Moncrief, 2002). Only recently, easy to use reliable passive sampling methods for NH_3 have been developed (Krupa and Legge, 1999a). In contrast, in the context of the occurrence of acidic precipitation, NH_4^+ concentrations in wet deposition have been measured by a number of major monitoring networks, both in Canada (Canadian Network for Sampling Acid Precipitation, CANSAP or Canadian Air and Precipitation Monitoring Network, CAPMoN) and in the US (National Atmospheric Deposition Program, NADP or the National Trends Network, NTN), as well as in other parts of the world (Krupa, 2002). However, improper sampling of precipitation can lead to significant underestimations of its NH_4^+ concentrations (Krupa, 2002).

In remote areas, NH_3 concentrations can be quite low, < 50 ppt (0.035 µg m^{-3}) (Lewin et al., 1986; Alkezweeny et al., 1986), whereas close to sources such as agricultural areas and cattle feedlot operations, they can be about three orders of magnitude larger. In Alberta, Legge et al. (1990a) in a two-year study found a mean background NH_3 concentration of 0.26 µg m^{-3} (0.37 ppb or 370 ppt). In contrast, in an agricultural area, the corresponding concentrations were 1.5 to 2.0 µg m^{-3} (2.16-2.88 ppb), with the maxima ranging from 8.3 to 11.9 µg m^{-3} (11.95-17.14 ppb) (Legge et al. 1990b). As a comparison, at Claremont, California, NH_3 concentrations ranged from 57 ppb (39.67 µg m^{-3}) when the winds were blowing from the direction of an agricultural area with a high density of cattle feedlots and poultry and dairy farms to undetectable levels (< 1-2 ppb or 0.70-.39 µg m^{-3}), when the wind was from other directions (Biermann et al., 1988). LeBel et al. (1991) reported NH_3 concentrations as high as 250 µg m^{-3} (360 ppb) during forest fires in Canada. Overall, in evaluating the significance of the air concentrations, it is important to realize that NH_3-N accumulates in the plant tissue (after correcting for translocation). Therefore, it is not just the air concentration, but also the duration of exposure that must be considered (see Table 2).

There are diurnal variations in atmospheric NH_3 concentrations. Temperature-driven NH_3 emissions reach their maxima during noon (Georgii and Lenhard, 1978; Ryden and McNeill, 1984; McInnes et al., 1986; Grünhage et al., 1990; Hatch et al., 1990; Van der Molen et al., 1990). In contrast, NH_3 accumulation occurs at night due to atmospheric inversions. Thus, concentration maxima occur at night in areas with low NH_3 emissions (Russell et al., 1983; Alkezweeny et al., 1986; Erisman et al., 1988; Wyers et al., 1992). These considerations are important in the context of NH_3 uptake by plant shoots (see Section 3, a, below).

Variation of NH_3 concentrations during the year is typically characterized by peaks in spring and summer (Georgii and Müller, 1974; Lenhard and Gravenhorst, 1980; Levine et al., 1980; Tjepkema and Cartica, 1981; Dawson, 1984; Vermetten et al., 1985; ApSimon et al., 1987; Erisman et al., 1987; Allen et al., 1988; Kruse et al., 1989), mainly caused by application of manure and fertilizer and by the increasing temperatures.

Diurnal variations in NH_4^+ (aerosol) concentrations follow the same pattern as for NH_3 (Stevens et al., 1978; Grünhage et al., 1990; Harrison and Allen, 1990). The same holds true for seasonal variation of NH_4^+ showing maxima in spring and summer, however, with a lower amplitude compared to NH_3 (Lenhard and Gravenhorst, 1980; Tjepkema and Cartica, 1981; Erisman et al., 1987).

During 1996-1999, in West Central Alberta mean fine particulate (size < 2.5 μm) NH_4^+ concentrations varied from 0.15 to 3.10 $\mu g\ m^{-3}$ (maxima 0.54-3.10 $\mu g\ m^{-3}$) (West Central Airshed Society, Drayton Valley, Alberta). In comparison, mean fine particle NH_4^+ concentrations varied from 0.52 to 1.09 $\mu g\ m^{-3}$ (maxima 3.97-10.07 $\mu g\ m^{-3}$) at six non-urban, agricultural or rural sites in the upper Midwestern USA (Pratt and Krupa, 1985).

At two sites near Calgary, Alberta, median NH_4^+ concentrations in precipitation varied from 0.65 to 0.90 mg L^{-1} and NO_3^- levels were 1.00-1.48 mg L^{-1} (Legge et al., 1990b). In comparison median NH_4^+ values (mg L^{-1}) were at: Chalk River (Ontario) 0.19-0.30; Cormack, B (Newfoundland) 0.04-0.06; Cree Lake (Saskatchewan) 0.05-0.06; Island Lake (Manitoba) 0.08-0.09 and Port Cartier (Quebec) 0.05-0.06. For the same sites median NO_3^- values were 2.04-2.17 (Chalk River); 0.27-0.35 (Cormack B); 0.18-0.40 (Cree Lake); 0.35-0.53 (Island Lake) and 0.58-1.73 (Port Cartier) (Legge and Krupa, 1990).

2.4 Deposition

Ammonia (NH_3), and subsequently derived NH_4^+ are removed from the atmosphere both by dry and wet deposition. Dry deposition occurs by diffusion (NH_3) and Brownian motion (fine particle NH_4^+) and to a much less extent by sedimentation or impaction (coarse particles, size > 2.5 μm). It is important to note that a major portion of NH_4^+ occurs in the fine particle fraction (Finlayson-Pitts and Pitts, 1999). In contrast, wet deposition occurs by rainout (in-cloud processes) and below cloud scavenging (washout). Ammonium salts such as $[(NH_4)_2SO_4]$ are hygroscopic and act as cloud condensation nuclei.

Dry deposition is more important in regions with high NH_3 emissions and wet deposition in areas with low emissions. However, this conclusion should be moderated, because of local variabilities in the precipitation depth. According to Kociuba (1984) results of a deposition model using SO_4^{2+} as an example showed that the ratio of dry to wet deposition in Alberta was 1.86. It is important to note that frequently SO_4^{2+} and NH_4^+ are well correlated in aerosols and in precipitation and therefore, should exhibit similar tendencies in their variability (Legge and Krupa, 1990) (see also the brief narrative in Sections 2, a and b). McVehil (1990) estimated by modeling, dry to wet NH_4^+ deposition ratios of 2.4 and 3.2 at two agricultural sites near Calgary, Alberta and a ratio of 0.8 for a high elevation forested site (Fortress Mountain, Alberta). McVehil also estimated mean values for total (dry + wet) NH_4^+ deposition of 6.5 kg ha^{-1} yr^{-1} and NO^{-3} deposition of 11 kg ha^{-1} yr^{-1} for southern Alberta.

Although comparisons between predicted and measured deposition values may be in good agreement (Derwent et al., 1989), model calculations may be quite erroneous because of several uncertainties in the input data. This is particularly true for emission data and for dry deposition velocities (V_d) which are highly variable depending among others on daytime-nighttime micrometeorological conditions such as wind characteristics, radiation, temperature, humidity, pH of the receptor and roughness of the surface (e.g., short grass, broad-leaved trees, conifers). Some data on V_d for NH_3 and NH_4^+ are listed in Table 1, suggesting that a reasonable range of V_d is 0.3-3 cm s^{-1} for NH_3 and values one order of magnitude lower for fine particle NH_4^+.

Furthermore, most deposition models do not reflect the high local scale variation mainly caused by differences in the receptor qualities of the canopies. Interception during dry deposition may significantly increase total NH_y deposition within plant canopies. In unpolluted stands, NH_y uptake within the plant canopy layer causes concentrations of NH_4^+ in canopy deposition (throughfall plus stemflow) to be lower than concentrations in bulk deposition (Verry and Timmons, 1977; Lindberg et al., 1986; Heil et al., 1987b, 1988, 1989). In polluted areas, canopy deposition is significantly greater than bulk deposition above the canopy (Van Breemen et al., 1982; Ivens et al., 1989; Van Dam et al., 1991; Bobbink et al., 1992a). Some data for different canopies are given in Table 2. Thus, regional scale models may significantly underestimate deposition to ecosystems with large canopy surfaces.

In addition, agro-ecosystems intensively fertilized with N may act as a source for NH_3 rather than as a sink. Grünhage et al. (1992) measured NH_3 flux of a fertilized grassland (240 kg N ha^{-1} yr^{-1}) by micrometeorological methods and found that annual NH_3 budget to be negative, i.e., NH_3 was emitted from the system on an annual time scale. Thus, if agricultural areas enriched with N are sources rather than sinks for NH_y (NH_3 + NH_4^+), deposition to an N poor ecosystem may be significantly higher than suggested by average deposition values from model calculations.

3.0 EFFECTS OF NH_3 AND NH_4^+ (NH_Y) ON VEGETATION

Both anthropogenic NH_3 and NH_4^+ derived from it, significantly influence N cycling in ecosystems (Fangmeier et al., 1994; Fenn et al., 1998). Since under field conditions the chronic effects of NH_3 and NH_4^+ are often difficult to distinguish, the two are considered together as NH_y.

Fangmeier et al. (1994) provided a state of the science review of the effects of NH_y on plants. The current knowledge of the effects of NH_y on plants is based on studies using a number of different approaches. These include experimental designs using artificial exposures to NH_3 or NH_4^+ either in controlled environment chambers, greenhouses, closed or open-top field chambers and chamber-less field studies where the physical and the chemical (pollution) climate are not controlled. For details on various exposure methods, the reader is referred to Manning and Krupa (1992). A summary of studies published within the past 20 years that provide information about the effects of NH_3 on plants is given in Table 3. In that table, results from fumigation experiments with known concentrations of NH_3 are included. Additionally, results of some field studies are provided where NH_3 was considered to be the major air pollutant, because of the vicinity of the study plots to the emission sources. The data summarized in Table 3 are listed according to the response parameters measured in the test plants and provide background information for the following sections on the NH_y effects on plants.

According to Fangmeier et al. (1994), NH_y effects on plants depend on several processes as illustrated in Figure 1: (a) uptake, (b) detoxification/assimilation, (c) development of injury when the amount of uptake exceeds detoxification, (d) metabolic changes related to detoxification/assimilation and (e) secondary effects following NH_y uptake and successful detoxification.

3.1 Uptake of NH_y by Shoots and by Roots

3.1.1 NH_3 (shoots)

Atmospheric NH_3 enters the leaves of higher plants almost exclusively through the stomata and is dissolved in the water film of the mesophyll cells to form NH_4^+ (Van Hove et al., 1987a). NH_3 flux into bean leaves (*Phaseolus vulgaris*) increased linearly with NH_3 concentration, and no mesophyll resistance to NH_3 uptake could be detected (Van Hove et al., 1987b). The cuticle was found to be nearly impermeable for NH_3 (Van Hove et al., 1987a,b, 1989b). Thus, NH_3 uptake directly follows stomatal conductance and therefore depends on the microclimate (radiation, air temperature, relative humidity, air turbulence and soil moisture availability) (Rogers and Aneja, 1980; Van Hove et al., 1990), internal CO_2 concentration, and plant water status (Hutchinson et al., 1972; Harper et al., 1989).

The driving force for NH_3 uptake is its concentration gradient between ambient air and the mesophyll tissue. As long as ambient NH_3 concentrations exceed the mesophyll concentration (compensation point), NH_3 uptake by the shoot will occur. However, at background ambient concentrations (approximately 1-10 $\mu g\ m^{-3}$ (1.44-14.4 ppb), i.e., 0.15-1.5 mPa), internal

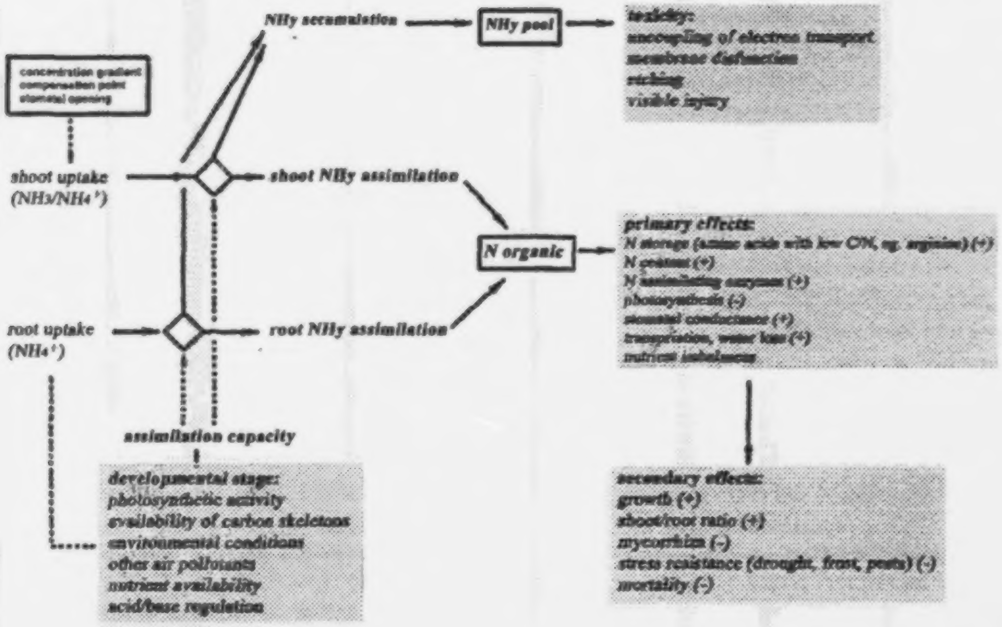
NHy accumulation
NHy pool
toxicity:
uncoupling of electron transport
membrane disfunction
etching
visible injury
concentration gradient
compensation point
stomatal opening
shoot uptake
(NH3/NH4+)
shoot NHy assimilation
N organic
primary effects:
N storage (amino acids with low C/N, eg. arginine) (+)
N content (+)
N assimilating enzymes (+)
photosynthesis (-)
stomatal conductance (+)
transpiration, water loss (+)
nutrient imbalances
root uptake
(NH4+)
root NHy assimilation
assimilation capacity
developmental stage:
photosynthetic activity
availability of carbon skeletons
environmental conditions
other air pollutants
nutrient availability
acid/base regulation
secondary effects:
growth (+)
shoot/root ratio (+)
mycorrhiza (-)
stress resistance (drought, frost, pests) (-)
mortality (-)

Figure 1 Pathways and factors governing the effects of NH_3 on plants. Source: modified from Fangmeier et al. (1994)

mesophyll NH_3 concentration may exceed ambient levels and cause emission of NH_3 from the plant. Internal mesophyll NH_3 concentration as is, approximates 0.25 mPa at 'normal' metabolism in beans (Farquhar et al., 1980) and may increase significantly during senescence, because of the destruction of proteins and amino acids (Stewart et al., 1987; Raven, 1988) or if plants are very well supplied with N through the use of fertilizers (Harper et al., 1987; Parton et al., 1988; Morgan and Parton, 1989; Schjoerring, 1991; Schjoerring et al., 1991). Calculations by Raven (1988) showed that at background concentrations NH_3 uptake by shoots may only play a minor role in N-nutrition of higher plants. However, elevated concentrations may significantly contribute to N-nutrition, as was shown by Faller (1972) in experiments with up to 1.6 mg m^{-3} (2.3 ppm) NH_3. In that case growth of sunflower continued to occur if NH_3 was the only nitrogen source. In experiments with *Lolium multiflorum* (ryegrass), foliar NH_3 uptake at 520µg m^{-3} (748 ppb) supplied 47.3% of total plant N at fertilization with 100 mg $^{15}NO_3$-N kg^{-1} and 35.2% at 200 mg $^{15}NO_3$-N kg^{-1} dry soil (Lockyer and Whitehead, 1986). Pérez-Soba and Van der Eerden (1993) exposed *Pinus sylvestris* L. (Scots pine) saplings to 0 and 50 µg m^{-3} (72 ppb) NH_3 and fertilized the saplings with $(NH_4)_2SO_4$ in the range of 0-200 kg ha^{-1} yr^{-1}. After four months of plant growth they found an increase in the N content of the needles of 49% by NH_3, while the increase due to fertilization with 200 kg ha^{-1} yr^{-1} was only 8%.

3.1.2 NH_4^+ (shoots)

NH_4^+ is accumulated on leaf surfaces both by dry and wet deposition (Gmur et al., 1983; Van Hove et al., 1989b; Bobbink et al., 1992a). Some comparisons between bulk deposition and throughfall of different canopies (grassland, heathland, forests) showed that an uptake of NH_4^+ by the canopies was accompanied by a release of K^+, Mg^{2+}, and Ca^{2+} (Lovett et al., 1985; Heil et al., 1987a, 1988; Ivens et al., 1987; Roelofs et al., 1987a; Alenas and Skärby, 1988; Leonardi and Flückiger, 1989; Garten and Hanson, 1990; Van Dam et al., 1991; Bobbink et al., 1992a). Foliar uptake of NH_4^+ is generally higher in grassland and heathland than in forest trees. The question of how NH_4^+ enters the leaves has not yet fully been answered. Wilson (1992) exposed branches of *Picea abies* (Norway spruce) and *Pinus sylvestris* (Scotch pine) to artificial rain solutions containing NH_4^+ or NO_3^-, and concluded that uptake was due to diffusion rather than H^+ or base cation exchange as commonly accepted. That conclusion should be tempered, because as opposed to solutions or precipitation, fine particle (size < 2.5 µm) deposition of NH_4^+ follows Brownian motion and not diffusion. Nevertheless, fine particles enter the leaf through stomata, same as NH_3 (Chevone et al., 1986), although that process may result in stomatal clogging.

3.1.3 NH_y (roots)

Normally root uptake of NH_3 does not occur since the NH_3 deposited to the soil is readily dissolved to yield NH_4^+. NH_4^+ in soils is less mobile than NO_3^-, but is easily accessible to plants under most conditions. The ratio of NO_3^- to NH_4^+ uptake depends on the pH of the soil (Bergback and Borg, 1989; Henry and Raper, 1989; Vessey et al., 1990), rooting zone temperature (Kafkafi, 1990; MacDuff and Jackson, 1991), rooting depth (Gijsman and De Willigen, 1991), mycorrhizal formation (Martin et al., 1986; Finlay et al., 1988; Marschner et al., 1991), ion concentration and the dominant type of nitrogen assimilation pathway of the plant species (Pearson and Stewart, 1993). NH_4^+ may prevent NO_3^- uptake and vice versa (Ullrich, 1987; Lee and Drew, 1989; Deignan and Lewis, 1988).

Uptake of NH_4^+ leads to acidification of the rooting zone, since it is exchanged with protons exuded by the roots (Tamm, 1991). Another problem arises from competition in the uptake between NH_4^+ and other cations such as K^+ (Lips et al., 1987; Vale et al., 1987). K^+ deficiency may occur in plants provided with NH_4^+ as sole N-source (Kinzel, 1982; Roelofs et al., 1985). NH_4^+ uptake via the roots may be reduced if shoot uptake of NH_y occurs. Pérez-Soba and Van der Eerden (1993) found decreased NH_4^+ sorption in roots of *Pinus sylvestris* (Scotch pine) when the shoots were fumigated with NH_3.

3.2 Assimilation and Detoxification of NH_y

NH_3 taken up by the shoots readily reaches equilibrium with NH_4^+ in the water film of the mesophyll tissue. There, NH_4^+ strongly dominates NH_3 and is assimilated, whereas NH_4^+ taken up from the soil is metabolized in the roots. Both in the roots and in the shoots, NH_4^+ assimilation takes place via the enzymes glutamine synthetase/glutamate synthase (GS/GOGAT) system (Lea and Miflin, 1974; Lewis et al., 1987; Stewart et al., 1987; Tischner, 1987; Valpuesta et al., 1987; Wallsgrove, 1987) (Figure 2). Although glutamate dehydrogenase is assumed to be an alternative for GS/GOGAT system (Srivastava and Singh, 1987), generally that enzyme plays a minor role in the assimilation of NH_y (Rhodes et al., 1989).

Two isoenzymic (isoenzymes are groups of enzymes that are very similar in their catalytic properties, but may be differentiated by the variations in their physical properties) forms of glutamine synthetase (GS) are found in plants: one common in chloroplasts of all species investigated and one in the cytoplasm of some species. The latter isoenzyme is thought to be responsible for NH_4^+ assimilation derived from photorespiration or from arginine decomposition by arginase or transaminases (Tischner, 1987). Glutamate synthase (GOGAT) exists in three isoenzymic forms dependent respectively on NADH, NADPH or ferredoxin that are found in the chloroplasts and in root cell plastids.

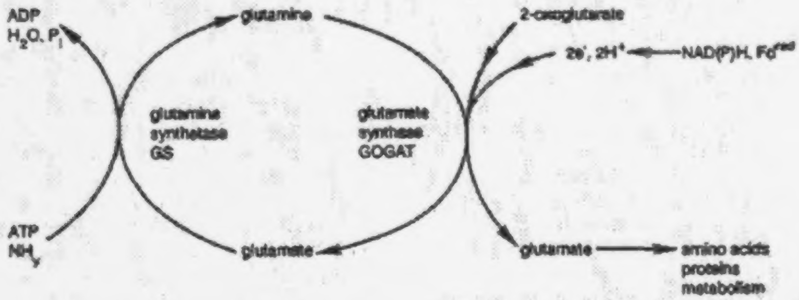

Figure 2 **Glutamine synthetase (GS) - Glutamate synthase (GOGAT) pathway of NH_3 assimilation in plants**

3.3 Metabolic Changes Due to NH_y Assimilation and Detoxification

NH_y detoxification may lead to significantly increased contents of organic nitrogen.

In *Calluna vulgaris* (heather) and *Deschampsia flexuosa* (hair-grass), the nitrogen content increased four-fold after exposure to 0.1 mg m^{-3} (144 ppb) NH_3 for 38 weeks (Van der Eerden et al., 1991). Increased N contents were also found in conifers both in fumigation experiments (Van der Eerden et al., 1989, 1992; Dueck et al., 1990) and in field studies near NH_3 sources (Van Dijk and Roelofs, 1988; Hofmann et al., 1990; Heinsdorf and Krauß, 1991). That was also true in tomato (*Lycopersicon esculentum)* and clover (*Trifolium pratense*) exposed to poultry farm emissions (Hauk et al., 1990). Increases in N content in conifer needles proved to be age dependent. The highest increases were found in current year needles, because of higher stomatal conductivity and higher metabolic activity in the younger tissue (Van der Eerden et al., 1989, 1992; Dueck et al., 1990; Van der Eerden and Pérez-Soba, 1992).

If NH_y uptake exceeds the assimilation capacity, NH_y will accumulate in the tissue resulting in toxic effects. Tissue accumulation of NH_y was observed in lettuce (*Lactuca sativa* var. *capitata*) and tomato following exposures to acute NH_3 concentrations, in controlled conditions (Van der Eerden, 1982; Hülsenberg, 1990) and in highly polluted conifer stands near livestock farms (Tesche and Schmidtchen, 1978; Heinsdorf and Krauß, 1991). Hofmann et al. (1990) distinguished three nutritional states in Scotch pine (*Pinus sylvestris)* according to the needle N content: (a) 'deficient', 1.0-1.8%, corresponding to the situation normally found in natural pine stands; (b) 'saturation', 1.8-2.35%, providing maximum growth and representing the physiological optimum (but not the ecological optimum which is below 1.8%); and (c) 'excess', 2.35-3.5%, causing growth reductions and in the long-term, injury. Stand stability decreases even at 2.0% nitrogen content.

Detoxification of NH_y is most effective if carbon skeletons are consumed as little as possible, i.e., if the nitrogen is stored in compounds with low C/N ratios. Indeed, alterations in the amino acid composition of plants exposed to NH_y reflect the attempts of the plants to detoxify NH_y most economically. Arginine with a C/N ratio of only 1.5 is one of the amino acids most significantly increased (up to 25-fold) when plants are exposed to NH_y (Van Dijk et al., 1992). Such results were obtained in the case of *Pinus sylvestris* fumigated with NH_3 (Pérez-Soba et al., 1990; Van der Eerden et al., 1990a) or growing close to fur farms (Pietilä et al., 1991), and with *Calluna vulgaris* near to a liquid manure storage facility (Steubing et al., 1991). In the latter experiment, however, *Deschampsia flexuosa* responded with increased concentrations of glutamine (C/N = 2.5) and asparagine (C/N = 2), but not arginine. Van Dijk and Roelofs (1988) found a 25-fold increase in arginine in needles of *Pinus sylvestris* injured from agricultural NH_y. According to Roelofs et al. (1987a,b) yellowing at the base of the youngest needles corresponds to extremely high arginine concentrations. Another amino acid, proline, is often increased by exposure to NH_y (Van Dijk et al., 1992). An elevated proline concentration is assumed to indicate drought stress.

In most cases, plants exposed to NH_y show increased concentrations of soluble proteins, as in *Picea abies* (Zedler et al., 1986), *Pinus sylvestris* (Pietilä et al., 1991), *Deschampsia flexuosa* and *Calluna vulgaris* (Steubing et al., 1991). Pietilä et al. (1991) reported alterations in the protein spectrum of *Pinus sylvestris* needles. Proteins with molecular weights 30, 38, 50, and 65-90 kd were absent in plants growing close to fur farms, probably causing reduced frost hardiness.

Besides alterations of specific amino acids or protein fractions, concentrations of most cellular compounds containing nitrogen tend to be increased. This also holds true for pigment contents. As long as the tissue is not injured, chlorophyll concentrations in plants exposed to NH_y increase, as in *Pinus sylvestris* (Pérez-Soba et al., 1990; Van der Eerden et al., 1990a), *Deschampsia flexuosa* and *Calluna vulgaris* (Steubing et al., 1991).

If NH_y applied via the shoot has to be detoxified, the enzymes responsible for assimilation, i.e. GS/GOGAT, should be more active. In the few experiments where glutamine synthetase activity in shoots was measured after NH_y exposure, increased GS activities were indeed observed in *Pinus sylvestris* (Pérez-Soba et al., 1990; Van der Eerden et al., 1990a) and in *Deschampsia flexuosa*, but not in *Calluna vulgaris* (Steubing et al., 1991).

NH_y uptake *per se* may lead to nutrient imbalances by increased nitrogen content and by growth increments accompanied by insufficiently increased uptake of nutrients other than nitrogen. This effect may be further increased by competition between root NH_y uptake and uptake of other cations such as K^+ and by leaching of K^+, Mg^{2+} and Ca^{2+} during shoot NH_4^+ uptake. However, no ion leaching was found when shoots of *Pseudotsuga menziesii* (Douglas fir) and *Calluna vulgaris* were fumigated with NH_3 (Van der Eerden et al., 1990a, 1992). Thus, variations in nutrient relations occur following NH_y exposure. Current year needles of *Pseudotsuga menziesii* fumigated with NH_3 showed decreased contents of K^+ and PO_4^- (Pérez-Soba et al., 1990), whereas Ca^{2+} and Mg^{2+} contents remained unchanged and no alteration in K^+, PO_4^-, Ca^{2+} or Mg^{2+} was detected in the previous year needles. Even if the nutrient contents remain unchanged after NH_3 exposure, as in *Pinus sylvestris* (Van der Eerden and Pérez-Soba, 1992), the N/ion ratios are altered since N contents increase after NH_y uptake. N/K, N/Mg and N/P ratios increased both in current and previous year needles in *Pseudotsuga menziesii* exposed to NH_3, however, the effects were more pronounced in current year needles (Van der Eerden et al., 1989, 1992). Field surveys in pine forests surrounded by intensive livestock operations showed the same type of nutrient imbalances (Van Dijk and Roelofs, 1988). Van Dijk et al. (1990) found mortality of up to 100% after a seven-month treatment of several conifer species with artificial rain containing 5,000 $\mu mol\ L^{-1}$ $(NH_4)_2SO_4$. They suggested that K^+ deficiency, rather than Al^{3+} toxicity, may have been the major cause of this mortality.

3.4 Changes in Leaf Gas Exchange Following Exposure to NH_y

Leaves of *Populus euramericana* (poplar) showed increased stomatal conductance after NH_3 exposure at $100 \mu g\ m^{-3}$ (144 ppb) for 6 or 8 weeks (Van Hove et al., 1989a). At the same time, the CO_2 assimilation rate, P_{max}, in particular was increased. Increased photosynthesis was also reported for *Pinus sylvestris* at exposures to $240\ \mu g\ m^{-3}$ (346 ppb) NH_3 (Van der Eerden et al., 1990b; Van der Eerden and Pérez-Soba, 1992). Van Hove et al. (1989a) assumed that higher demand for carbon skeletons resulting from NH_3 assimilation was responsible for increased CO_2 fixation and increased stomatal conductance to be regulated by internal CO_2 concentration, whereas NH_3 itself had no direct influence on stomatal conductance. Thus, NH_3 uptake may cause an autocatalytic increase of further NH_3 flux into the leaves by inducing stomatal opening via the internal CO_2 level, as long as photon flux density is sufficient for equivalent photosynthesis (Van der Eerden and Pérez-Soba, 1992).

Whether or not dark respiration responds to NH_y remains unclear. Van Hove et al. (1989a, 1991) did not observe NH_3 effects on dark respiration of *Populus euramericana*, whereas *Pinus sylvestris* showed significantly enhanced dark respiration after fumigation with NH_3 (Van der Eerden and Pérez-Soba, 1992).

Stomatal opening induced by NH_3 caused higher transpiration rates and thus, altered water relations. Transpiration increased significantly in *Pinus sylvestris* saplings exposed to NH_3 in climate chambers and branch water potential decreased (i.e., became more negative) after drought stress for 10 days, compared to the control plants (Van der Eerden et al., 1990b; Van der Eerden and Pérez-Soba, 1992). Similar results have been obtained by Dueck et al. (1990), by using open-top chambers to expose *Pinus sylvestris* saplings to NH_3.

3.4.1 Effects of NH_y onEepicuticular Waxes

NH_y entering the leaves via the stomata may affect mesophyll processes, but NH_y may also directly alter the cuticle. Needles of *Pseudotsuga menziesii* (Douglas fir) exposed to NH_3 in climate controlled growth chambers (Van der Eerden et al., 1992), in open-top chambers (Thijse and Baas, 1990) and tree stands polluted with NH_y (Thijse and Baas, 1990) showed erosion of the crystalline wax structures. Erosion also occurs naturally during needle aging, however, it was enhanced by NH_3 in the experiments. In contrast, no significant effects were found on wax erosion (e.g., building of amorphous wax) in *Pinus sylvestris* needles exposed to NH_3 at 60 or 100 $\mu g\ m^{-3}$ (86 or 144 ppb) for nine months (Bacic et al., 1992) or in *Populus euramericana* leaves fumigated for seven weeks at 64 $\mu g\ m^{-3}$ (92 ppb) (Van Hove et al., 1991).

Although experimental results show that NH_y can damage the epicuticular wax layer, that effect is difficult to assess under field conditions, because of natural fluctuations in growth, aging, wax re-crystallization, presence of other air pollutants and stress factors and high intra-species variation.

3.4.2 Factors Determining the Toxicity of NH_y

NH_y may: (a) function as an electron acceptor, thus causing uncoupling of electron transport along membranes (Losada and Arnon, 1963); (b) saturate membrane lipids, thus causing membrane dysfunction (Van der Eerden, 1982) and (c) cause direct leaf etching and necrosis (death) at very high concentrations (Van der Eerden et al., 1990c). Since NH_y may not be stored in the tissues without damage, plants readily try to assimilate NH_y to form organic nitrogen compounds. Thus, primary toxicity of NH_y arises as soon as uptake exceeds assimilation capacity.

The plant's capacity to detoxify (i.e., to assimilate) NH_y depends on several internal and external parameters. Internally, NH_y assimilation requires carbon skeletons, energy (ATP), and reduction equivalents (NAD(P)H, ferredoxin). Thus, high rates of NH_y assimilation may be expected at growth stages with high metabolic activity; generally external conditions (irradiation, temperature, water supply) favoring high rates of photosynthesis.

The influence of the developmental stage of the tissue on NH_y detoxification capacity is important. According to Tesche and Schmidtchen (1978) NH_3 pollution near livestock farms resulted in shedding of older conifer needles before the younger needles were injured. Greenhouse fumigations with acute concentrations of NH_3 (2-2.8 mg m^{-3} or 2.9-4.0 ppm) caused injury first to the older needles of *Pinus sylvestris*, *P. nigra* (Austrian pine) and *P. mugo* (Mugo pine) (Ewert, 1979). Age dependent reactions of conifer needles were also found at NH_3 concentrations lower than the acute levels. Increased N content after NH_3 fumigation were only observed in the current year needles of Douglas fir (*Pseudotsuga menziesii*) (Van der Eerden et al., 1989, 1992) and *Pinus sylvestris* (Dueck et al., 1990). Likewise, needle biomass increased only in current year flushes of *Pinus sylvestris* fumigated with NH_3 (Van der Eerden et al., 1990b; Van der Eerden and Pérez-Soba, 1992).

At conditions limiting photosynthetic capacity and thus, availability of carbon skeletons and energy, NH_y proved to be more toxic than under more favorable conditions. For example, Van der Eerden (1982) exposed tomato (*Lycopersicon esculentum*) to 2 mg m^{-3} (2.9 ppm) NH_3 and found foliar injury after 24 h in the dark, but not in the light. Similar effects were observed at low temperatures limiting metabolism in general and thereby reducing NH_y assimilatory capacity. Conifers exposed to NH_3 in the field near a pig farm or fumigated in open-top field chambers were injured only during wintertime (fumigation concentration: 0.25 mg m^{-3} or 360 ppb) and not in the spring (fumigation concentration: 0.54 mg m^{-3} or 778 ppb) (Van der Eerden, 1982).

The potential of NH_y to cause metabolic disturbance is also a function of the type of nitrogen nutrition of a particular species. Pearson and Stewart (1993) developed a concept called the 'leaf metabolic vitality theory' to divide plants into groups with differing susceptibility to NH_y. This was based on their leaf acid–base regulation, which is related to the type of nitrogen nutrition. Plants may be roughly divided into three groups: those preferring NO_3^-, those preferring NH_4^+, and those using both NO_3^- and NH_4^+. Most fast growing annual species, among them most agricultural crops (Kinzel, 1982; Malhi et al., 1988), and fast growing pioneer trees such as *Betula* spp. (birch), *Populus* spp. or *Sambucus nigra* (black elderberry) prefer NO_3^- (Pearson and Stewart, 1993), whereas slow growing perennial species mainly prefer NH_4^+. *Ericaceae* (e.g., *Calluna* spp.; *Erica* spp., and *Vaccinium* spp., bilberry, blueberry, etc.), conifers, climax species among broad-leaved trees such as *Quercus* spp. (oak), *Fagus sylvatica* (beech), and *Carpinus betulus* (hornbeam), and an exception among crops, rice (*Oryza sativa*) (because of the anaerobic soil conditions) belong to the latter group (Van den Driessche and Dangerfield, 1975; Kinzel, 1982; Blacquière et al., 1988; Magalhaes and Huber, 1991; Pearson and Stewart, 1993). Plants preferring NO_3^- may further be divided into those assimilating nitrate in the roots, in the shoots, or both in the roots and shoots.

Raven (1988) calculated that assimilation of 1 mol NH_4^+, irrespective of root or shoot uptake, forms 1.33 mol H^+, and NH_3 forms 0.33 mol H^+, in the synthesis of core metabolites. Taking into account the assimilation of S from sulfate and P from phosphate resulting in production of some OH^-, excess H^+ production is 1.22 mol H^+, when 1 mol NH_4^+ is assimilated, and 0.22 mol H^+ when 1 mol of NH_3 is assimilated (Raven, 1988). On the other hand, 0.78 mol excess OH^- is yielded when 1 mol NO_3^- is reduced to form amino groups (Raven, 1988).

Plants may easily get rid of H^+ resulting from NH_y uptake and assimilation, if these processes take place in the roots, by excreting H^+ into the soil (however, with the consequence of further increasing the acidity of the rooting zone). On the other hand, it seems unlikely that H^+ may readily be removed from shoots (Raven, 1988; Pearson and Stewart, 1993). Thus, even small amounts of H^+ from shoot NH_y uptake and assimilation may disturb acid-base balance in leaves (Pearson and Stewart, 1993). Those species preferring nitrate uptake and transport into the leaves for assimilation, however, may buffer significant amounts of H^+ by OH^- production from NO_3^- assimilation and are expected to be more tolerant to foliar uptake of NH_y (Pearson and Stewart, 1993).

3.5 Direct Toxicity of NH_y and Visible Foliar Injury

Accidental releases of NH_3 from industrial processes or during its transport are known. In most of these cases, the concentrations will be extremely high and the exposure time will be very short. In these episodes the dominant cause of injury is a direct chemical 'etching' of the foliage (Temple et al., 1979; De Temmerman, 1980). Table 4 provides a listing of plants considered to be sensitive, intermediate or tolerant to NH_3 exposures, based on foliar injury symptoms. The order of sensitivity among plant species, for the types of exposures resulting in injury symptoms, is different from the order at lower concentrations over longer periods. For instance, for short-term exposures conifers are highly resistant (Temple et al., 1979), while for longer exposures they are relatively sensitive (Van der Eerden, 1982).

Generally, the assimilation capacity of the plant species determines the degree of injury. If the assimilation capacity is not sufficiently high to detoxify NH_y, acute (visible) injuries may occur. On broad-leafed plants acute exposures to anhydrous NH_3 will result in the death of the leaf tissue between the veins (inter-veinal necrosis) (Figures 3 and 4). This can be easily confused with similar symptoms caused by acute exposures to sulphur dioxide (SO_2) (Krupa and Legge, 1999b; also see Jacobson and Hill, 1970; Flagler, 1998). Several cereals and grasses show chlorotic (yellow) and necrotic (dark tan to brown) inter-veinal streaking.

In Europe, field observations have been made by a number of investigators, mostly on trees in the vicinity of NH_3 sources such as livestock farms, manure storage facilities or fertilizer plants (Kühne, 1966; Garber and Schürmann, 1971; Scholl, 1975; Ewert, 1978a,b; Hunger, 1978; Tesche and Schmidtchen, 1978; Schulz, 1980; Rudolph, 1981; Van der Eerden et al., 1981; Van der Eerden, 1982; Sun, 1989; Kaupenjohann et al., 1989; Kaupenjohann, 1990; Hofmann and Heinsdorf, 1990; Heinsdorf and Krauß, 1991). Conifers near livestock farms usually respond to NH_3 by needle necrosis (death) starting at the tips of the oldest needles, subsequently with needle loss and finally with the death of the tree. In the former GDR (East Germany), in the vicinity of huge pig farms with up to 200,000 pigs, forest decline areas of 2,000 ha attributable to NH_3 have been observed (Hofmann and Heinsdorf, 1990). Roelofs et al. (1987a,b) defined four types of visible NH_y injury on *Pinus sylvestris*: (a) red or brown needle discolouration (insufficient NH_y detoxification); (b) yellowing of needles, occurring more frequently in older needles (K^+ and/or Mg^{2+} deficiency); (c) yellowing of the youngest needles, most pronounced at the needle base (extremely high arginine content); and (d) occurrence of fungal or insect diseases (nutrient imbalance).

Controlled exposures in greenhouses with acute NH_3 concentrations (2-28 mg m^{-3}) showed that injury symptoms differ with plant species (Ewert, 1979). Broad-leaved trees mainly displayed black discoloration of the leaves, whereas conifers mostly displayed brown needle necrosis. Van der Eerden (1982) described sharply bordered necrotic tips of older needles of *Taxus baccata* (yew) to be specific for NH_3. However, in most cases leaf injury from acute NH_3 concentrations may not easily be distinguished from symptoms caused by other stresses (Van der Eerden, 1982).

Visible symptoms observed on plant organs other than leaves include reduced flowering in *Arnica montana* (mountain tobacco) after fumigation with NH_3 at 0.053 mg m^{-3} (76 ppb) for 15 months (Van der Eerden et al., 1991), reduced number of flowers by 50% in *Petunia hybrida* (petunia) exposed to acute NH_3 concentrations (> 2 mg m^{-3} or > 2.9 ppm) for two weeks (Van Haut et al., 1979) and empty ear development in oat (*Avena sativa*) exposed to poultry farm emissions containing NH_3 at 2.3-3.9 mg m^{-3} (3.3-5.6 ppm) (Hauk et al., 1990).

Epiphytic lichens growing on tree trunks can be used as biological indicators of acute anhydrous NH_3 exposures. Lichens contain complex organic acids (lichenic acids). These acids react with anhydrous NH_3, conferring a purple coloration to the lichens within 1-2 days after exposure (Figure 4 B).

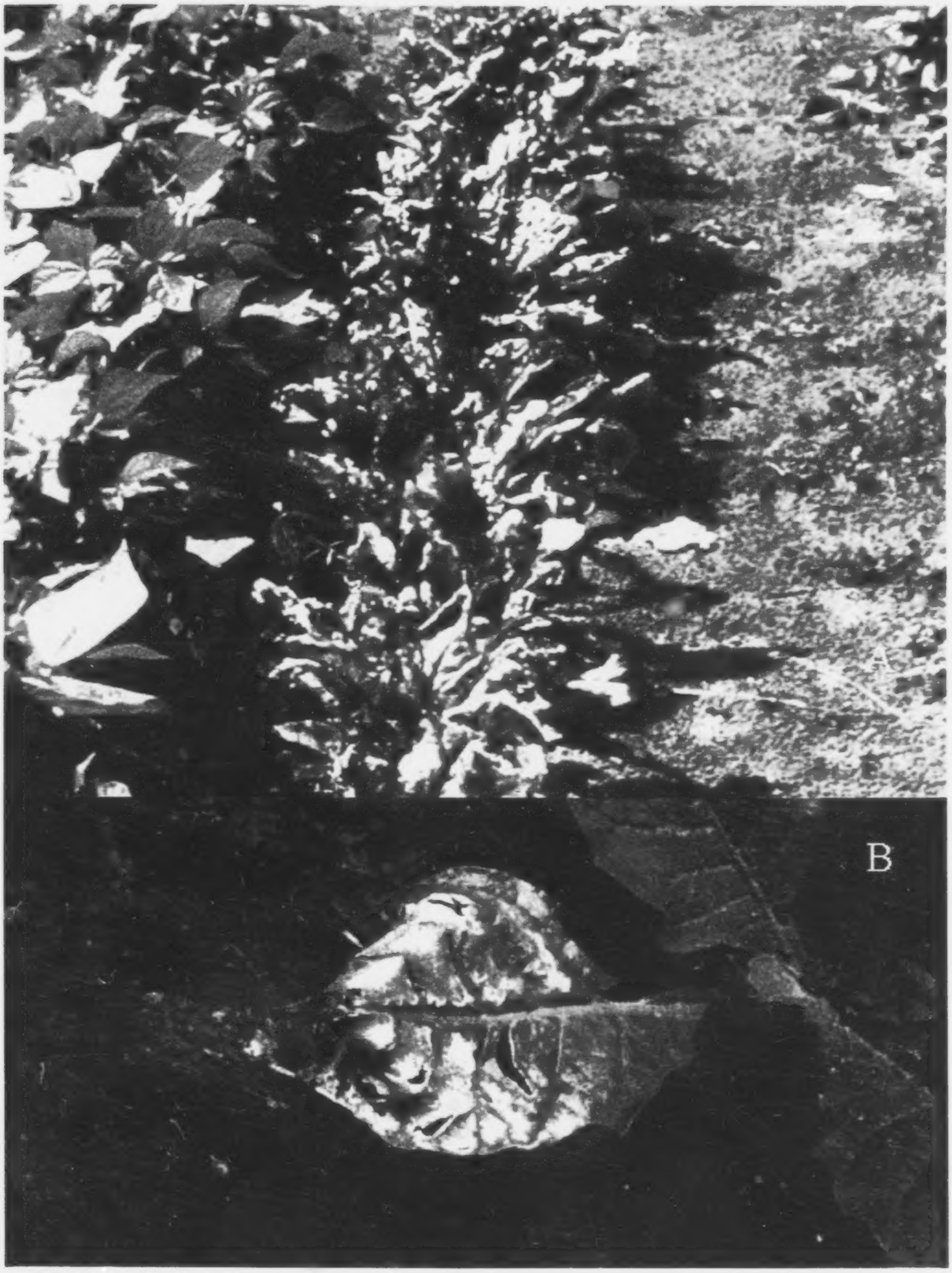

Figure 3 (A). Row of table beet (*Beta vulgaris*) exposed to acute (relatively high) anhydrous NH_3 concentrations due to an industrial malfunction. (B). Close-up of a table beet leaf showing acute response to anhydrous NH_3. Note the death of the leaf tissue (brown areas) between the veins. These symptoms are very similar to those induced by acute exposure to SO_2

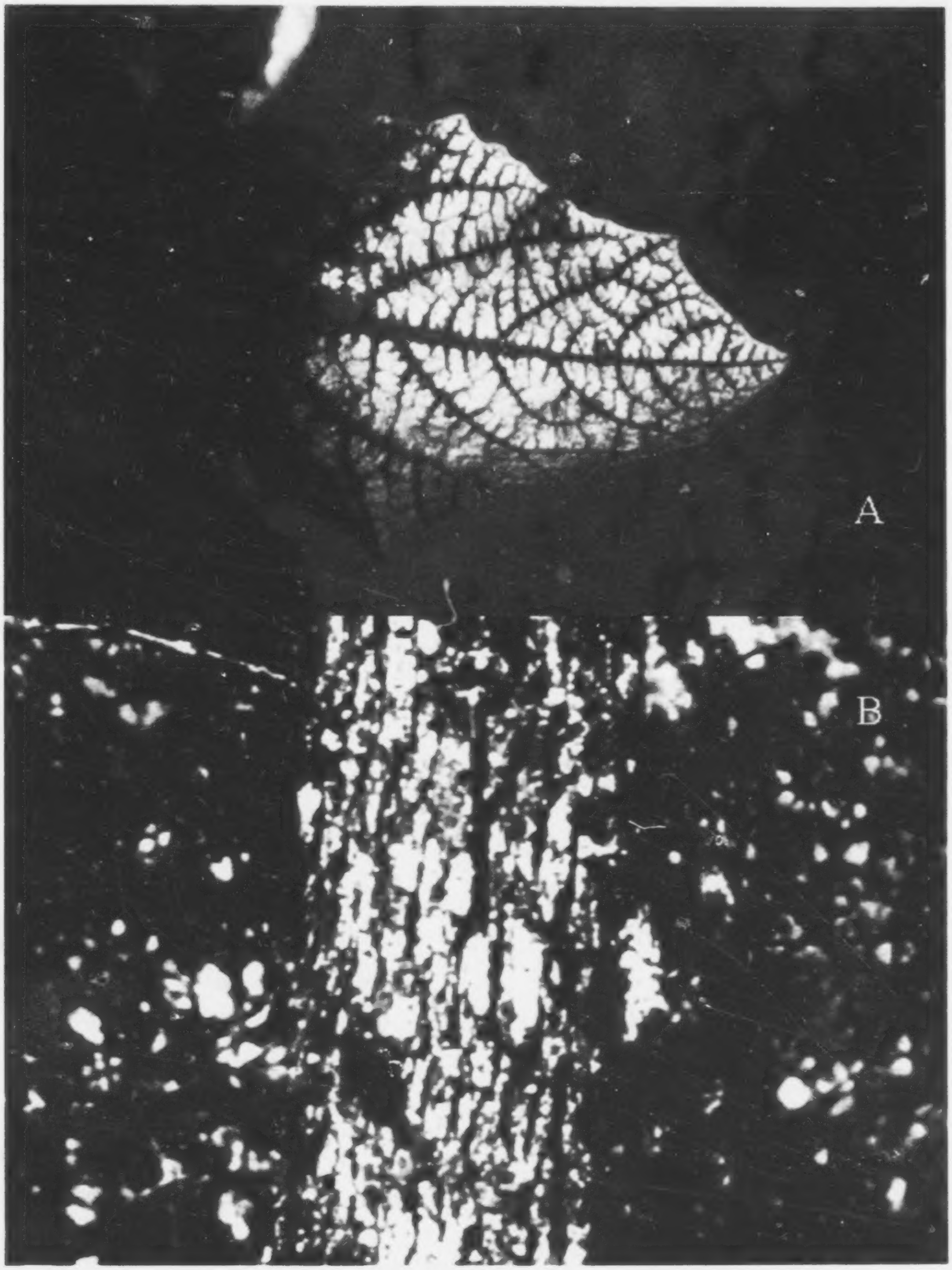

Figure 4 (A) Cherry tomato (*Lycopersicon esculentum* var. *cerasiforme*) showing acute response (white bleached areas between the veins) to anhydrous NH_3. (B). Epiphytic lichens on the trunk of an oak tree exhibiting purple colouration due to acute exposure to anhydrous NH_3. This response can be used as a biological indicator of NH_3 pollution

4.0 SECONDARY EFFECTS OF NH_Y UPTAKE AND ASSIMILATION ON VEGETATION

4.1 Growth Responses

One of the most obvious plant responses that might be regarded as 'secondary' effect after NH_y assimilation, is enhanced growth. This should not be surprising since nitrogen must be regarded as a limiting factor (in the sense of biomass production) for plant growth in most (natural) habitats. Enhanced growth has been observed in many experiments as long as the NH_y concentrations were not toxic. At acute (toxic) NH_3 concentrations, however, growth is depressed (Van Haut et al., 1979; Van der Eerden, 1982; Hülsenberg, 1990).

Whenever increased growth is observed after NH_y application that is mainly due to the shoot growth response. Root growth increases only a little or at least less than shoot growth, leading to higher shoot/root ratios (Encke, 1986). This has been shown for both gaseous NH_3 and NH_4^+ in precipitation. Increased shoot/root ratios were observed following NH_3 exposures in several species such as *Agrostis capillaris* (bentgrass), *Arnica montana* (Van der Eerden et al., 1990a), *Calluna vulgaris* (Van der Eerden et al., 1990a,c, 1991), *Deschampsia flexuosa* (Dueck et al., 1991), *Potentilla erecta* (tormentil), *Viola canina* (dog violet) (Van der Eerden et al., 1990a) and *Pinus sylvestris* (Van der Eerden et al., 1990b; Van der Eerden and Pérez-Soba, 1992). After a seven-month treatment with artificial rain containing $(NH_4)_2SO_4$, Van Dijk et al. (1990) found no influence on the total biomass production, but an increase in the ratios of shoot/root and coarse/fine roots. Field observations showed that the fine root content in the soil of pine forests decreased close to pig farms (Hofmann and Heinsdorf, 1990).

Competition between root growth and NH_y assimilation as sinks for carbon skeletons is likely responsible for altered shoot/root ratios after NH_y uptake. Shoot uptake of NH_y will keep photosynthetic primary products in the shoot, whereas root uptake of NH_y will increase the demand for NH_4^+ acceptor molecules and inhibit the synthesis of structural root compounds and may even lead to conversion of structural compounds into NH_4^+ acceptor molecules (Lewis et al., 1987).

Thus, enhanced growth caused by NH_y uptake may not necessarily be regarded as beneficial but rather as detrimental, if other effects such as decreased resistance to environmental stress as described in the following section are considered. Some experimental findings indicate that growth enhancement may turn into increased mortality of plants at a later developmental stage or during environmental stress. Dueck (1990) found a 20% reduction of the survival rate of *Calluna vulgaris* seedlings that had been fumigated with NH_3 at 53 or 105 $\mu g\ m^{-3}$ (76 or 151 ppb) for eight months. Survival of *Antennaria dioica* (cat's-foot) was reduced by 30% at the same concentrations applied for 16 months and *Arnica montana* by 50% (Van der Eerden et al., 1991). The authors explained the high mortality of *Arnica montana* as due to an altered shoot/root ratio, resulting in a higher susceptibility to environmental stresses.

4.2 Resistance to Stress

4.2.1 Drought Resistance

Van der Eerden and Pérez-Soba (1992) exposed *Pinus sylvestris* saplings to NH_3 at up to 240 µg m^{-3} (346 ppb) for three months. Water loss and transpiration drastically increased in fumigated plants and branch water potential decreased (i.e., became more negative) significantly after withholding water for 10-14 days from the plants. Similar results were obtained with *Calluna vulgaris* plants which experienced irreversible drought injury after fumigation with 240 µg m^{-3} (346 ppb) NH_3 and drought stress for 10 days, whereas controls and plants exposed to lower NH_3 concentrations were able to recover from drought stress (Van der Eerden et al., 1991).

That NH_y may decrease the resistance to drought stress may be explained by at least two mechanisms (Fangmeier et al., 1994). First, the demand for carbon skeletons to assimilate NH_y increases CO_2 uptake and thus, stomatal opening and water loss. Secondly, since shoot growth is more enhanced by NH_y than root growth, water supply from the roots may easily become insufficient during periods of drought.

4.2.2 Frost Resistance

Several studies with conifers suggest that NH_y may reduce frost hardiness. NH_3 at 105 µg m^{-3} (151 ppb) applied in open-top chambers increased frost sensitivity (measured as electrolyte leaching) of *Pinus sylvestris* needles exposed at -10°C (Dueck et al., 1990; Van der Eerden et al., 1990b). Dueck et al. (1990) believe that NH_3 at low to moderate concentrations prolongs the growth phase in autumn and causes winter hardiness to develop too late, which may have detrimental consequences if first frost periods occur early in the year. These findings are supported by field observations by Pietilä et al. (1991), who reported dieback of *Pinus sylvestris* during the winter in the vicinity of fur farms and by De Temmerman et al. (1987) who observed that frost injury significantly contributed to *Pinus sylvestris* dieback in Belgium and such injury was most pronounced near NH_3 sources (livestock management, fields intensively sprayed with liquid manure). Misting of red spruce (*Picea rubens*) with $(NH_4)_2SO_4$ for seven months decreased frost hardiness at the end of October (Cape et al., 1991).

4.2.3 Insect Pests

Most insect pests may attack their hosts more successfully at nitrogen levels in the host tissue higher than those usually found under field conditions. Increased nitrogen content caused by NH_y uptake may thus weaken the host defense against pests. In addition, altered foliar C:N ratios in the plant may influence herbivory, as with N fertilization (Krupa et al., 1998). Pest/host interaction at elevated NH_y pollution has been studied intensively with the heather beetle (*Lochmaea suturalis)*, the larvae of which prey on leaves of *Calluna vulgaris*. Van der Eerden et al. (1991) exposed *Calluna vulgaris* to NH_3 at concentrations between 4 and 107 µg m^{-3} (5.8 and 154 ppb) for 12 months and fed the beetle larvae with leaves harvested from those plants. There was an increase in the number of larvae reaching the third (last) and most injurious instar (growth stage) with increasing pre-exposure NH_3 level to the plants. Similar results were obtained when *Calluna vulgaris* was exposed for 15 months to artificial rain containing different levels of $(NH_4)_2SO_4$. In that experiment, the percentage of third instar larvae shed from the plants rose with increasing $(NH_4)_2$ SO_4 concentrations (Van der Eerden et al., 1990a). Larval development and adult beetle weight were enhanced in plots fertilized with 400 kg ha^{-1} NPK (56 kg N ha^{-1}) (Heil, 1984).

4.2.4 Pathogens

Several field observations indicate that trees are more susceptible to fungal infection under high nitrogen status (irrespective of the form and path of nitrogen enrichment, i.e. NH_y or NO_x, fertilizer application or atmospheric deposition) or altered nutrient balance such as increased N/K ratios (Ylimartimo, 1991). Roelofs et al. (1985) found that pine trees (*Pinus nigra* var. *maritima*) infected with *Brunchorstia pinea* or *Diplodia pinea* had higher needle N content than uninfected trees. The authors conclude that NH_y deposition from agricultural sources was responsible for elevated N content of the needles. In Belgium and The Netherlands, pine die-back near NH_3 sources was accompanied by infection with *Spheropsis sapinea*, most pronounced at close distances to intensive livestock operations or fields intensively sprayed with liquid manure (De Temmerman et al., 1987; Van Dijk et al., 1992).

Pinus sylvestris stands in Finland fertilized with NPK showed severe injury caused by infection with *Ascocalyx abietina* (Vasander and Lindholm, 1985). The authors suggest nitrogen application caused late winter hardening, frost injury and subsequent weakening of the trees leading to fungal infection. Similar results were obtained in *Pinus radiata* (Australian pine) fertilized with 100 or 400 kg N ha^{-1} yr^{-1} resulting in increased arginine content and consequent infection with *Dothistroma* sp. correlating well with the arginine content (Lambert, 1986).

4.3 Mycorrhizae

Mycorrhizae are symbiotic associations between plant roots and fungi. Mycorrhizal associations are found virtually in every higher plant family (Harley, 1969). Those associations result in a number of benefits to the host plant: (1) longevity of the fine roots; (2) increased rate of nutrient absorption from the soil; (3) selective absorption of certain ions from the soil; (4) improved nutrient cycling; (5) resistance to certain root pathogens; (6) increased tolerance to soil toxins, cold temperatures, and high temperatures; and (7) tolerance to adverse soil pH and excess cations and anions (Hayman, 1978; Marx and Krupa, 1978). With the exception of the nutrient relationships and to a degree resistance to pathogens, mechanisms governing the other benefits are not well understood.

Symbiotic fungal infection of plant roots and successful mycorrhizal development depends on the supply of carbohydrates from the host to the fungus. In return, the fungus supplies the host with otherwise limiting nutrients, including N. There is evidence that plants adapted to N limiting soils (e.g., conifers, members of the cucumber family) have evolved with an N conservation mechanism, ornithine or urea cycle in their root system. While most amino acids contain one atom of N, intermediates in the ornithine cycle such as citrulline and arginine contain 2 and 3 N atoms per molecule. In the absence of mycorrhizal association, this cycle becomes non-operational due to mineral deficiency and more importantly, because the bi-product of the conversion of arginine to ornithine, urea, is toxic to higher plants. Mycorrhizal infection resulting in sufficient supply of minerals to the host roots removes the blockage of the ornithine cycle leading to the availability of additional N and efficient amino acid metabolism and protein biosynthesis in the root. Equally importantly, most microorganisms including mycorrhizal fungi have the enzyme urease that detoxifies the urea released during the conversion of arginine to ornithine, the latter leading to the formation of glutamate, a key amino acid (Krupa et al., 1973; Krupa and Bränström, 1974) (also see section 3, b and Figure 2 in this chapter).

As discussed earlier, NH_y assimilation requires carbon skeletons and may thus compete with mycorrhizal sinks and inhibit mycorrhizal development and growth. Since mycorrhizae are of great importance for ion uptake, nutrient imbalances caused by NH_y uptake may further be increased (Bledsoe and Rygiewicz, 1986). It is well known that fertilization of forest stands can reduce mycorrhizal development (Menge and Grand, 1978). Therefore, it has been suggested that atmospheric nitrogen deposition has similar effects as fertilizer application (Nihlgård, 1985).

Reduction in mycorrhizae after NH_y exposure has been reported in several studies. Van der Eerden et al. (1992) found a distinct reduction of mycorrhizal infection in roots of *Pseudotsuga menziesii* exposed to NH_3. Roots of *Calluna vulgaris* fertilized with 0, 40, 80 or 120 kg N ha^{-1} exhibited significantly decreased mycorrhizal infection (Mickel et al., 1991). Field observations in pine forests near to huge pig farms showed a decline in mycorrhizal frequency in the upper soil horizon and a reduction of vital mycorrhizal cells (Hofmann and Heinsdorf, 1990). Heijne et al. (1992) tested the reaction of *Antennaria dioica*, *Arnica montana* and *Hieracium pilosella* (mouse-ear hawkweed) to $(NH_4)_2SO_4$ in greenhouse and field experiments. They found the percent vesicular-arbuscular mycorrhizal (VAM) infection to increase in *Antennaria dioica*, remain unchanged in *Hieracium pilosella* and decrease in *Arnica montana*, a species found to decline in Dutch heathlands, after two years of field exposure to $(NH_4)_2SO_4$.

5.0 INTERACTIVE OR JOINT EFFECTS OF NH_Y WITH OTHER AIR POLLUTANTS ON VEGETATION

Very few experiments have been conducted to study the combined effects of NH_3 with other air pollutants such as SO_2 or ozone (O_3). Since one of the effects of O_3 is to accelerate leaf senescence (Pell et al., 1997), and conversely since NH_y is known to prolong the growth period and retard senescence (Fangmeier et al., 1994), one might expect O_3 and NH_y to negate the effects of each other. However, the modes of action of these two pollutants are completely different. The toxic effects of O_3 *per se* are dependent on the amount of uptake and detoxification by the antioxidant defense system of the plants (Pell et al., 1997). Since the antioxidant systems require energy to operate, even successful detoxification of O_3 may increase the plant sensitivity to NH_y by decreasing the amount of energy available for NH_y assimilation. Another aspect to be considered is that NH_3 exposure tends to cause stomatal opening. Thus the amount of O_3 uptake may be increased in the presence of NH_3.

Van der Eerden et al. (1989) exposed Douglas fir saplings to NH_3 and O_3 and did not observe any visible injury, however, the pollutant combination caused erosion of the epicuticular wax layer. Both NH_3 and O_3 altered the plant nutrient (K, Mg and P) content. Van der Eerden et al. (1994) exposed an O_3-sensitive bean cultivar to a range of O_3 concentrations with and without the addition of NH_3. Leaf injury by O_3 was reduced in the presence of NH_3, while biomass production was stimulated by NH_3 and reduced by O_3 with no statistically relevant interaction.

Sulphur dioxide and NH_y are deposited together, since the deposition of one compound is enhanced by the other (Adema et al., 1986; Van Hove et al., 1989b; McLeod et al., 1990; Bobbink et al., 1992a; Dueck and Elderson, 1992) and the two pollutants may be thus expected to act synergistically. Photosynthesis in *Populus euramericana* saplings exposed to NH_3 and SO_2, however, showed an antagonistic response; it was increased by NH_3, and that effect was cancelled by a combination with SO_2 (Van Hove et al., 1991).

Synergistic effects were found in several experiments with heathland species exposed to NH_3 and SO_2 in open-top chambers. Mortality of *Calluna vulgaris* seedlings after long-term fumigation with NH_3 and SO_2 increased synergistically (Dueck, 1990) and frost resistance of *Pinus sylvestris* decreased and needle injury was increased (Dueck et al., 1990). In this experiment, smoothening of epicuticular waxes of *Pinus sylvestris* needles was observed only when NH_3 and SO_2 were present together and not after exposure to either pollutant alone.

Dueck and Elderson (1992) exposed *Arnica montana* and *Viola canina*, as mono and mixed cultures with *Agrostis capillaris*, to 90 $\mu g\ m^{-3}$ (34 ppb) SO_2 and 50 $\mu g\ m^{-3}$ (72 ppb) NH_3, singly and in combination, and studied the effects of the fumigants on competitive ability and plant nutrient status. No interactions between the two pollutants were found on growth parameters with one exception; the root biomass of *Agrostis capillaris* was reduced in a less than additive manner. However, nutrient content (S, N, P, K, Ca, Mg) in some cases was affected in more than an additive manner by SO_2 and NH_3 The same holds true for example, for an increase of root N content in *Arnica montana* and *Agrostis capillaris* and shoot K^+ content in *Viola canina.*

In summary, the amount of available information on the interactive effects of NH_3 and NH_y must be considered as too small to draw any general conclusions.

6.0 EFFECTS OF N DEPOSITION AT THE ECOSYSTEM LEVEL

Anthropogenic N input affects its status and cycling in ecosystems both through the soil and plant canopy deposition, leading to eutrophication of coastal marine waters (Burkart and James, 1999), and to acidification of the soils (Fenn et al., 1998) (also Figure 5). Since natural terrestrial ecosystems are usually N deficient (most of the N pool originates from N_2-fixation rather than from weathering and is present as organic N), excess N from deposition is readily taken up and accumulated until saturation occurs. According to Tamm (1991), ecosystems in the saturation phase are characterized by an amount of N supply meeting all their requirements, with simultaneous leaching of NO_3^-. It is clear that N deposition has steadily increased during roughly the past 100 years, so that most ecosystems are assumed to be in the accumulation or already in the saturation phase.

Ecological modification and successional change by means of N deposition will be most obvious in systems poor in N, because species adapted to N deficiency will soon be out-competed by species with higher N demand (Aerts, 1990; Tilman and Wedin, 1991). Therefore, species diversity may be severely reduced by nitrogen eutrophication (Ellenberg, 1985). Besides eutrophication, acidification may cause floristic alterations, as was shown in deciduous forests (Falkengren-Grerup, 1986, 1989) or in heathlands (Roelofs, 1986). Overall, nitrogen deposition may have severe consequences for species diversity and nature conservation (Woodin and Farmer, 1993). For example, many of the threatened species in central Europe are most abundant in semi-natural systems (e.g., species-rich grasslands, heathlands), the maintenance of which is dependent on management (aspects relevant to the removal of nutrients). Current management practices, however, do not provide any mechanisms to protect these systems from atmospheric deposition (Woodin and Farmer, 1993).

6.1 Soil Processes

Nitrogen saturation and acidification of the soil are symptoms of changes in a complex network of interacting processes that are influenced by atmospheric input and indirectly by effects on vegetation and soil microflora and microfauna. The population of soil microfauna generally declines due to acidification and as a consequence decomposition and mineralization of organic matter slows down (Van Straalen et al., 1988). Decomposition and mineralization of organic material is also influenced by N deposition via its impact on biomass production and the chemical composition of the vegetation (Berendse, 1990).

6.1.1 N Saturation

Unfertilized terrestrial ecosystems are usually characterized by relatively closed N cycling, i.e., N input and output are comparably small in relation to N exchange within the soil/plant subsystem (Fenn et al., 1998). In these ecosystems, N is usually limiting for productivity and additional nitrogen is readily absorbed and utilized. If deposition exceeds the capacity to utilize N for a considerable period of time, over-saturation of the system (Tamm, 1991) indicated by N loss (Nilsson et al., 1988; Tamm, 1989; Rosén et al., 1992) will occur. N loss may occur either by leaching of NO_3^- which is more mobile than NH_4^+ (Grennfelt and Hultberg, 1986) or by

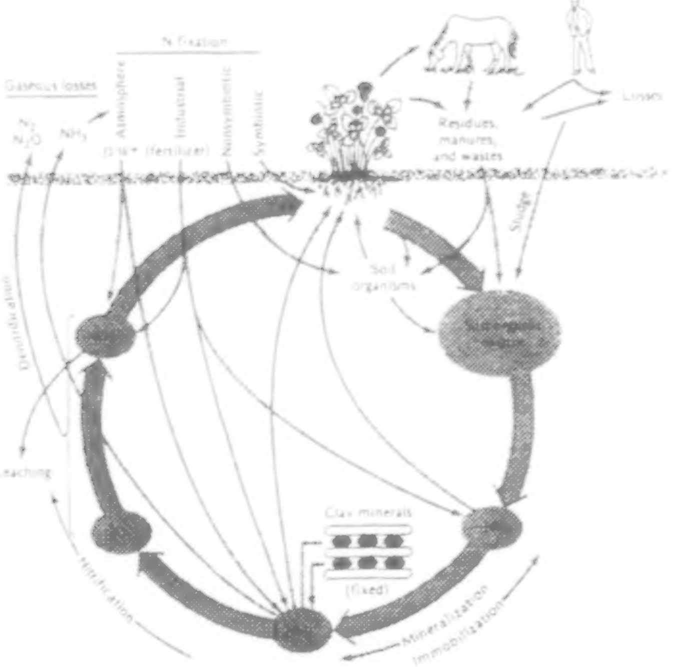
Animals
Humans
N fixation
Gaseous losses
N_2
N_2O
NH_3
Atmosphere
Industrial
Nonsymbiotic
Symbiotic
D/W* (fertilizer)
Residues, manures, and wastes
Losses
Sludge
Soil organisms
Soil organic matter
Denitrification
Leaching
Nitrification
Clay minerals
(fixed)
Mineralization
Immobilization

Figure 5 The nitrogen cycle, emphasizing the primary biological transformations (large shaded circle) the means of replenishment and the losses from the soil. Chemical fertilizers from industrial nitrogen fixation are an increasingly important source of this element, but excessive use has serious environmental implications. D/W = Respectively, dry and wet atmospheric deposition. Source: modified from Brady (1990)

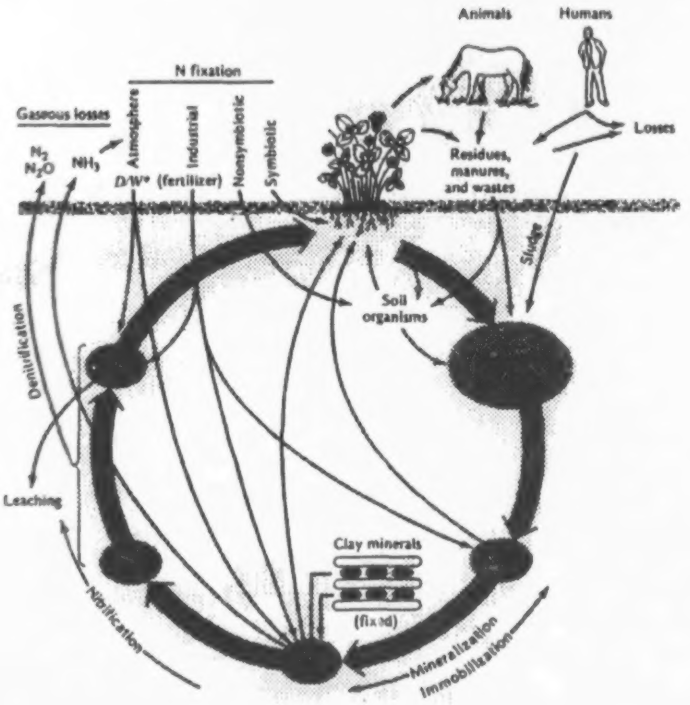
Animals
Humans
N fixation
Gaseous losses
N_2
N_2O
NH_3
Atmosphere
Industrial
Nonsymbiotic
Symbiotic
D/W*
(fertilizer)
Losses
Residues, manures, and wastes
Sludge
Soil organisms
Denitrification
Leaching
Clay minerals
(fixed)
Nitrification
Mineralization
Immobilization

Figure 5 **The nitrogen cycle, emphasizing the primary biological transformations (large shaded circle) the means of replenishment and the losses from the soil. Chemical fertilizers from industrial nitrogen fixation are an increasingly important source of this element, but excessive use has serious environmental implications. D/W = Respectively, dry and wet atmospheric deposition. Source: modified from Brady (1990)**

denitrification, yielding N_2 and some N_2O. The latter gas is emitted at higher rates from soils polluted with NH_4^+ (Magalhaes et al., 1984; Tietema and Verstraten, 1991) and contributes to the greenhouse effect and the destruction of the stratospheric ozone layer (Houghton et al., 1990).

According to Fenn et al. (1998) there are several N saturated forests in North America Table 5). Among those is Turkey Lakes Watershed in Ontario. Nitrogen saturation is thought to progress through three stages as N inputs increase in the forest (Aber et al., 1989). Stage 0 is the typical condition of N limitation. Stage 1 occurs when N concentrations in the foliage and possibly in tree production increase and brief periods of N losses from the system are temporarily amplified. In stage 2, N losses from the forest are sustained and nitrification increases. In most cases, reports of N saturation pertain to stage 2. In stage 3, chronic N inputs lead to forest decline or decreased productivity. For a detailed discussion of N excess in the North American forest ecosystems, predisposing factors and the ecosystem responses, the reader should consult Fenn et al. (1998).

In Canada, the highest N deposition and NO_3^- concentrations in surface waters occur in southcentral Ontario and southwestern Quebec. The highest N deposition (13 kg N ha^{-1} yr^{-1}) is moderate compared to the high deposition areas in Europe and the US (Jeffries, 1995). Lac Laflamme in Quebec and Turkey Lakes in Ontario exhibit NO_3^- export patterns of stages 1 and 2 respectively of watershed N saturation (as per Stoddard, 1994). Moderate NO_3^- export to lakes occurs in many watersheds in southeastern Canada. In regions with the lowest N deposition (Newfoundland and Labrador), NO_3^- concentrations in the lakes are near zero (Jeffries, 1995).

6.1.2 Acidification

NH_4^+ deposited to the soil may either be taken up by plant roots or be subjected to nitrification yielding NO_3^- (Figure 5). Since both processes result in proton release into the soil, acidification will occur, particularly in acid soils with low buffering capacity. Subsequently leaching of cations such as K^+, Ca^{2+} and Mg^{2+} leading to nutrient imbalances for plant growth and release of toxic ions such as Al^{3+} may occur (Van Breemen et al., 1984; Reuss et al., 1987; Nilsson et al., 1988; Van Dijk et al., 1989; Tomlinson, 1991).

The acidifying potential of nitrogen may be calculated as (NH_4^+ input + NO_3^- output) - (NH_4^+ output + NO_3^- input) assuming a negligible change in storage of NH_4^+ and NO_3^- in the soil system. If this term yields values greater than zero, acidification is to be expected (Prinz, 1990).

6.2 Ecosystem Responses

6.2.1 Effects on Heathlands

The most obvious vegetation change in Dutch heathlands during the past decades has been their transition into grassland (Heil and Diemont, 1983), both in dry (dominated by *Calluna vulgaris*) and wet heathlands (dominated by *Erica tetralix*, cross-leaved heath). Similar vegetation changes were observed in northern Germany (Steubing and Buchwald, 1989).

These vegetation changes in heathlands have been intensively studied, and much evidence is available now from both field observations and exposures with model plant communities showing that transition of heathland into grassland is induced even at low levels of N deposition.

Calluna vulgaris or *Erica tetralix* may successfully compete with grasses even at high rates of N deposition as long as the canopies are closed, providing only insufficient solar radiation for new seedlings to emerge (Aerts et al., 1990). However, N deposition causes nutrient imbalances, increases the shoot/root ratio and, thus, increases the sensitivity of the dwarf-shrubs to drought stress, frost stress, and heather beetle attack (Heil and Diemont, 1983; Heil, 1984; Van der Eerden et al., 1991). These processes lead to gaps in the canopy, which then may be readily invaded by grasses that are more efficient in utilizing additional N, gaining a competitive advantage. Grasses replacing dwarf-shrubs have been shown to utilize NH_3 better than *Calluna vulgaris* (growth enhancement: *Molinia caerulea*, moor grass > *Deschampsia flexuosa* > *Calluna vulgaris* (Van der Eerden et al., 1990a). After NH_3 exposure, both shoot and root growth of *Deschampsia flexuosa* was increased, whereas *Calluna vulgaris* responded only with the shoot growth (Van der Eerden et al., 1991). Similarly allocation of NH_3 from the shoots into the roots was significantly greater in *Deschampsia flexuosa* than in *Calluna vulgaris* (Dueck et al., 1991). Long-term fumigations with NH_3 caused mortality in *Calluna vulgaris*, not observed in *Deschampsia flexuosa* and *Molinia caerulea* (Van der Eerden et al., 1991). In general, grasses appear to have higher nutrient-use efficiency than dwarf-shrubs, as was shown by Aerts (1990) who compared nutrient-use efficiency of *Erica tetralix*, *Calluna vulgaris* and *Molinia caerulea*.

Besides weakening the competitive abilities of dominating dwarf-shrubs, N deposition, in particular NH_y by its acidifying effects, was responsible for a decrease in species diversity in heathlands (Van Breemen and Van Dijk, 1988). Acidification from NH_y deposition may lead to the disappearance of species-rich microhabitats with higher pH, thus threatening species such as *Thymus serpyllum* (thyme) or *Pedicularis sylvatica* (lousewort) (Roelofs, 1986; Roelofs et al., 1987a). Acidification is also held responsible for the decline of *Arnica montana* (and other species of the *Viola canina* group) in Dutch heathlands, since it is well correlated with low soil pH, low levels of available base cations and high Al^{3+}/Ca^{2+} ratios (Fennema, 1992).

Drastic alterations have been reported in cryptogamic (flowerless, seedless plants) vegetation of Dutch heathlands. Van Ree and De Smidt (1989) compared recordings of moss and lichen flora in the province of Gelderland from 1965 to 1975 with mappings in 1988 and found that 25 cryptogamic species have been nearly or completely lost. Average moss cover declined from 50-60% in 1965-1975 to 2-10% in 1988 within the heathland areas. This is attributed both to direct effects of eutrophication, as well as to an increase of dense grass canopies preventing moss growth. Drastic loss in species was observed in liverworts, with only 3 of the 13 species found in 1965-1975 still being present in 1988. In a similar manner, 12 of the 18 lichen species commonly found have disappeared or become rare.

6.2.2 Effects on Species-rich Grasslands

Associations of the Mesobromion (meadow) related species belong to the plant communities with the greatest species diversity known in central Europe. Many threatened species adapted to low nutrient availability are common in the Mesobromion group. The conservation of these calcareous grasslands demands regular management (mowing and removal of the hay) to keep the nutrient status at a low level.

In Dutch calcareous grasslands, an increase in dominance of *Brachypodium pinnatum* (false-brome) was observed during the past decade (Bobbink, 1991). The dominance of *Brachypodium* *pinnatum*, however, is negatively correlated with species diversity in these systems (Bobbink and Willems, 1987). In fertilizer experiments with N, P or K and NPK, growth and competitive ability of *Brachypodium pinnatum* were significantly increased by N or NPK addition (Bobbink, 1991). The grass species benefited from N input more than other chalkland species without suffering from lowered P availability caused by N-induced growth stimulation. Thus, N deposition severely reduces species diversity in calcareous grasslands by promoting the dominance of *Brachypodium pinnatum*.

6.2.3 Effects on Forests

Until the 1980-1990s, the 'classical' forest decline theories such as due to SO_2 pollution or acidic rain were most popular. However, at the present time, it is well accepted that forest decline is a result of complex interactions of both of natural and anthropogenic stresses. These include climatic events, e.g., early or late frost, drought periods and biotic stress such as pathogens and pests, management practices, air pollution, and possibly global climate change (McLaughlin, 1985; Krause et al., 1986; Klein and Perkins, 1988; Innes and Oleksyn, 2000).

Nihlgård (1985) was the first to consider N deposition from NH_y and NO_x as significant contributors to forest decline in Europe. Taking into account all the direct and indirect effects of N deposition previously described and considering the receptor qualities of forest canopies to atmospheric deposition, N deposition must indeed be regarded as a factor severely disturbing nutrient cycling in forest ecosystems with detrimental effects for tree health.

While some of the N deposited on tree canopies is directly taken up, the rest accumulates on canopy surfaces, contributing to the throughfall deposition (Lindberg et al., 1986). Forest canopy N deposition by far exceeds bulk deposition above the canopy and deposition to forest edges again exceeds deposition into the closed forest (Grennfelt and Hasselrot, 1987). Even in areas like southern Sweden that are nearly exclusively polluted by long range transport, average N deposition to forests is approximately 20 kg ha^{-1} yr^{-1}, with extreme values greater than 40 kg ha^{-1} yr^{-1} (Grennfelt and Hultberg, 1986). At these amounts of deposition, NO_3^- leaching from the system has already been observed, indicating that N saturation has taken place.

The decline of Norway spruce forests in northern Bavaria (Fichtelgebirge) subjected to different types of pollutants has been mainly attributed to nutrient imbalances (Schulze, 1989). In that geographic area, gaseous pollutants such as SO_2, NO_2, and O_3, in spite of being present at rather high concentrations, had no long-lasting direct effects on needle physiology (e.g., gas exchange). Soil chemistry and plant nutrition, however, were significantly altered by deposition of SO_4^{2+}, NO_3^-, and NH_4^+ causing N/cation imbalance in the tissue, with severe secondary effects.

Areas highly polluted with N are found in The Netherlands, Belgium (De Temmerman et al., 1987), and areas of northern Germany and at least by 1990 in East Germany when many intensively managed livestock operations were shut down. N deposition in the forests in Netherlands is typically around 80 kg N ha^{-1} yr^{-1} (Houdijk and Roelofs, 1991) and deposition of 115 kg ha^{-1} yr^{-1} was found in Douglas fir stands at a distance of 30 km from intensively managed agricultural areas, 83% resulting from NH_y deposition and 17% from NO_x deposition (Draaijers et al., 1989; Ivens et al., 1989). Acidification leading to the leaching of NO_3^- and cations and release of Al^{3+} occurs in the acidic soils that are mainly impoverished in nutrients and low in their buffering capacity (Van Breemen et al., 1982; Van Breemen and Van Dijk, 1988), thus severely reducing the vitality of the trees.

Detailed investigations on the decline of pine forests around intensively managed livestock operations have been carried out near Eberswalde (former East Germany), where a farm with up to 20,000 pigs was in operation until 1991 (Hofmann and Heinsdorf, 1990; Hofmann et al., 1990; Heinsdorf and Krauß, 1991). Canopy N deposition in these Scotch pine forests was up to 150 kg ha^{-1} yr^{-1}. The forests showed distinct zonation with particular injury symptoms dependent on the distance from the source. At greater distances, N accumulation resulted in increased tree growth, followed by areas with N saturation as indicated by the N content of the needles above 1.8%. Closer to the source, further increase of N deposition resulted in soil acidification, leaching of cations, fine root destruction, reduction in mycorrhizae and development of visible needle injury, further enhanced by direct effects of NH_3 present at toxic levels. At distances less than approximately 1 km from the source, the forests were completely destroyed. Dwarf shrubs such as *Calluna vulgaris* and *Vaccinium vitis-idaea* normally occurring in these forests disappeared and the grasses *Calamogrostis epigeios* (reedgrass) (at sites naturally somewhat more enriched with nutrients) or *Deschampsia flexuosa* (at poor sites) dramatically increased in their coverage. Since the grass layer may compete with pine for water supply, further susceptibility to drought stress, in particular because of the dry climate in this region, occurred as an indirect effect of N deposition. Besides changes in the herb layer, invasion of shrubs such as *Prunus serotina* (black cherry) and *Sambucus nigra* is visibly promoted in these pine stands.

Overall tree vitality is likely a relatively insensitive indicator for N saturation effects on the forest ecosystem. More sensitive indicators are species composition of the herbaceous (Steubing and Fangmeier, 1991) and epiphytic vegetation, including bryophytes, lichens and the mycorrhizal fungi.

7.0 EFFECTS OF N DEPOSITION ON EPIPHYTIC LICHENS AND GREEN ALGAE

7.1 Lichens

Since the publication of Nylander (1866), epiphytic or tree bark inhabiting lichens (seedless, flowerless lower plants, products of symbiosis between algae and fungi) have been used in air pollution mapping studies (Haugsjå, 1930; Henderson, 1995a,b, 1996a,b, 1997a,b, 1998). Hawksworth and Rose (1970) developed a scale for estimating SO_2 concentrations from the observed lichen species.

Different epiphytic lichen assemblages are found on tree barks that are acidic or nutrient-poor (e.g., oak and beech) and neutral or nutrient-rich or "eutrophicated" (e.g., willow, elm and poplar) (Van Dobben and Ter Braak, 1998). Lichens in the first category are defined as "acidophytic", while those in the second category are defined as "nitrophytic" (Brand et al., 1988; Wirth, 1991). The scale of Hawksworth and Rose (1970) also distinguishes between "acidic" and "eutrophicated" bark.

Van Dobben and Ter Braak (1999) studied the relationships between measured concentrations of SO_2, NO_2 and NH_3 and lichen abundance in the Netherlands (Table 6). They compared the observed relationships to published indicator scales of lichen sensitivity to air pollution. For SO_2, a good agreement was found between all the indicator scales and calculated sensitivities based on the presence or absence of a given species. For NO_2 and NH_3 the correspondence was less obvious. The sensitivity to NH_3 was inversely related to the Wirth's (1991) acidity indicator scale. Species that react positively to NH_3, tended to be sensitive to SO_2 and NO_2.

Although at the outset, increases in the abundance of "nitrophytic" lichens may appear to be correlated with increases in N deposition, such lichen species appear to have become more common with decreases in SO_2 concentrations and/or S deposition (acidification) (Poikolainen et al., 1998a; Van Dobben and Ter Braak, 1998).

Van Dobben and Ter Braak (1998) proposed three hypothetical mechanisms to explain the strong increase in the "nitrophytic" lichens in responses to decreasing SO_2 concentrations:

- Decreasing SO_2 concentrations may have resulted in an upward trend in bark pH. "Nitrophytic" lichens prefer high bark pH.

- "Nitrophytic" lichen species appear to be more sensitive to SO_2 than others.

- "Nitrophytic" lichen species respond more rapidly than others to sudden decreases in SO_2 concentrations. This suggests that under ameliorating conditions, "nitrophytic" species can colonize new sites more rapidly than others.

There are fundamental differences in the effects of atmospheric SO_2 and NH_3 on terrestrial higher plants and epiphytic lichens (Table 7). Nevertheless, in environmental research, conclusions are frequently based on univariate studies. But, under ambient real world conditions, it is difficult to separate the influence of many interacting variables. Although lichens can be used as excellent indicators of environmental stress, the value of epiphytic lichens as accumulators of air pollutants, have not been exploited by biological effects scientists in studies of source apportionment (Sloof, 1995). Until such studies are fully expanded, it would be difficult to establish more definitive cause-effect relationships.

7.2 Green Algae

As noted previously in this report, N deposition has a two fold ecological impact. 1. N causes acidification of the soil due to leaching of base cations and 2. It is a vital plant nutrient, which in excess causes eutrophication. It has been observed that increased N deposition resulted in changes in vegetation, especially in areas of high deposition in Central Europe, to the extent eutrophic plant species have increased at the expense of oligotrophic species (Bobbink et al., 1992c; Sutton et al., 1993). At the same time, epiphytic algae have increased especially on Norway spruce (*Picea abies*) needles in the southern parts of Fenno-scandia and in Central Europe (Göransson, 1988, 1990; Bråkenhielm and Liu Qinghong, 1995).

Poikolainen et al. (1998b) reported an increased abundance of epiphytic green algae on conifers in Finland during 1985-1995. Abundance of green algae was the highest in southern Finland where N deposition is highest. According to the authors, the abundance of green algae may have been caused by several concurrent changes in the environment. A slight increase in mean annual temperature, a long-term stability in N deposition and a clear decrease in S deposition may all have contributed to the increased growth and abundance of green algae. At a local scale, variations in the microclimate due to nutrient richness of the habitat, the predominant tree species, stand age and density, all have an effect. As in the case of lichens, multi-variate, source apportionment studies are required to better explain the relationships between N deposition and the distributions of epiphytic green algae.

8.0 AIR QUALITY INDICATORS FOR PROTECTING VEGETATION

The critical level/critical load concept has been followed in many countries since over some two decades and has been widely accepted as an appropriate tool to provide estimates of target levels/target loads for decision makers (Bull, 1991).

8.1 Critical Levels

Critical levels are defined as 'the concentrations of pollutants in the atmosphere above which direct adverse effects on receptors, such as plants, ecosystems or materials may occur according to present knowledge' (UNECE, 1988).

8.2 Critical Loads

Critical loads concept was originally developed in Canada in the 1970s. Critical loads are defined as 'A quantitative estimate of an exposure to one or more pollutants below which harmful effects on specified sensitive elements of the environment do not occur according to present knowledge' (Nilsson and Grennfelt, 1988).

There is inevitably some debate on how to define 'adverse or harmful effects'. In particular, this is true for NH_3 that acts as a fertilizer at low concentrations without any detectable (primary) toxic effects. However, secondary effects such as increased susceptibility to stress or altered competitive ability (mostly not investigated or not detected in short term experiments) may occur. Nevertheless, the United Nations Economic Commission for Europe (UNECE, 1994) has adopted the critical loads approach.

8.2.1 Critical Levels (NH_3)

Table 8 provides a listing of critical levels for NH_3 given by different investigators. The values obtained by Van der Eerden (1982) and Posthumus in UNECE (1988) were estimated using the 'envelope' method, i.e., by a graphical approach plotting all data from NH_3 exposures causing adverse effects in a concentration/time frame and fitting a curve directly below the lowest effective exposure levels. According to Fangmeier et al. (1994), that approach, however, may not be appropriate for several reasons. First, one has to take into account that the data used, originated from very diverse experimental approaches. The sensitivity of plants to air pollutants significantly differs depending on the (climatic and experimental) exposure conditions. Plants grown under constant growth conditions in controlled environment chambers or in greenhouses usually differ in their sensitivity from plants grown outside and hardened by diurnal climatic variation. Secondly, since experimental designs usually include the exposure of plants to certain concentrations for certain periods of time, the true lowest concentration or duration of exposure causing adverse effects will not be correctly determined, since the entire response surface is not being defined. Using eco-toxicological models that include repair and compensation factors may yield more appropriate results. Van der Eerden et al. (1991) used a toxicological model described for water pollution by Kooijman (1987) and for soil pollution by Van Straalen and Denneman (1989) to recalculate critical levels for NH_3. Those values are shown in Table 8 and are far below the previous estimates.

Fangmeier et al. (1994) tried to apply the ecotoxicological model to estimate critical levels for four different groups of plants: (a) natural vegetation as a whole, (b) most sensitive species such as members of the *Viola canina* group and mosses, (c) trees and (d) agricultural crops (Hadwiger-Fangmeier et al., 1992). However, the amount of available data (observations) was too small in many cases, to calculate critical levels for NH_3 for corresponding plant groups. Nevertheless, the range of susceptibility to NH_3 was suggested to be: natural vegetation > forests > crops, assuming forests to include managed systems and natural vegetation to include native woodlands.

More recently, Van der Eerden et al. (1998) provided an estimate of the risk of NH_3 damage to sensitive crops in relation to the distance to the source, based on the mean and variations in the emissions, plume dispersion, regional background concentration, landscape characteristics and plant sensitivity. The results of the application of the model NOEL (No Observable Effect Levels) are presented in Figure 6. The reliability of the method was determined by the quality of the information or data used and the authors state that several possibilities for over- or under estimations exist and discuss various precautions that should be taken in applying their model.

8.2.2 Critical Loads (N)

Examples of estimates and model calculations of critical loads of N are presented in Table 9. In many cases (particularly in Europe), current N deposition by far exceeds those critical load values. In a 1996 report by the Danish Environmental Protection Agency (full English translation not available, see http://www2.mst.dk/magazile/issue1/ammonia2/fakta1.htm), critical loads stipulated for ammonia and other N species was 5 and 10 kg ha^{-1} $yr^{-1}$for heaths and bogs respectively. For forests, 10-20 kg ha^{-1} yr^{-1}, depending on the soil conditions. According to the report, if N deposition were evenly distributed across entire Denmark, it would equal an average of 21 kg ha^{-1} yr^{-1}, with 14 kg attributable to NH_3 and the remaining 7 kg to NO_x (primarily fossil fuel combustion).

Natural and semi-natural ecosystems, as well as forests must be expected to be severely at risk from the current amount of N deposition. Agricultural crops appear to be the only systems not negatively influenced at present, since high productivity and turnover prevent the accumulation of N. In the overall analysis, one should keep in mind, however, that N_2O release to the atmosphere and NO_3^- leaching into the ground water by agricultural systems represent serious problems, which may be increased by N deposition into these systems.

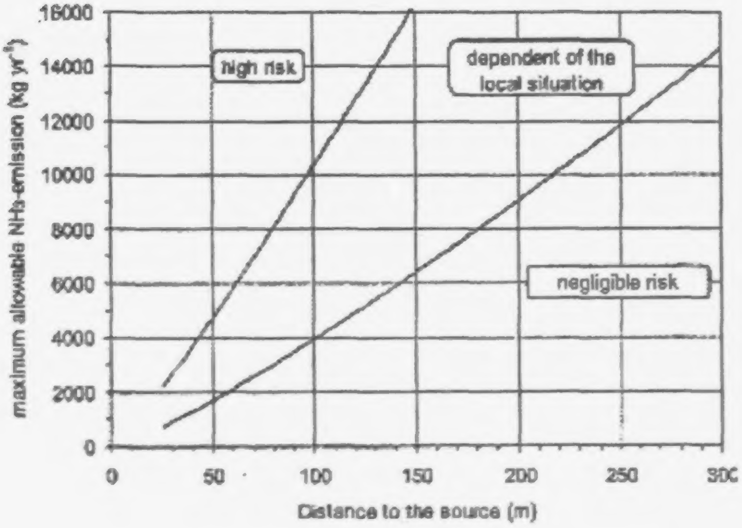

Figure 6 Modeled relationships between the maximum NH_3 emissions, with no exceedances of the 'no observable effect level' and distance between the source and a sensitive receptor. Area above the upper curve indicates that the emissions are too high or the source is at a too short a distance from the sensitive receptor. The lower curve indicates situations where the prevailing wind direction is from the source to the sensitive receptor. While the lower curve reflects high background NH_3 concentrations, the upper curve reflects the opposite. Source: Van der Eerden et al. (1998)